A NEW SYNTHETIC METHODOLOGY APPLIED TO THE PREPARATION OF SOME NOVEL, ALKYL SUBSTITUTED, CYCLIC CARBENE COMPLEXES OF RUTHENIUM, TUNGSTEN, AND RHENIUM.

By

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Abstract of Dissertation Presented to the Graduate School
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A NEW SYNTHETIC METHODOLOGY APPLIED TO THE PREPARATION OF SOME NOVEL, ALKYL SUBSTITUTED, CYCLIC CARBENE COMPLEXES OF RUTHENIUM, TUNGSTEN, AND RHENIUM

By

Rhonda Lee Trace

August 1991

Chairperson: William M. Jones
Major Department: Chemistry

It has been shown that 1-carbonyl(h^5-cyclopentadienyl)(2-methoxy)-1-ferracyclopentene can be formed by a 1,2 alkyl migration reaction through the decarbonylation of (dicarbonyl)(h^5-cyclopentadienyl)(1-methoxy-1-cyclobutyl)iron. This novel rearrangement has also been found with similar compounds of manganese.

With the intent to observe this reaction in complexes with metal centers in the second and third row of the periodic table, the synthesis of (dicarbonyl)(h^5-cyclopentadienyl)(1-methoxybenzocyclobutenoyl-1-carbonyl)ruthenium was attempted. Subsequent decarbonylation of this acyl complex was unsuccessful, therefore, the carbene complex had to made by an alternative method. The migratory insertion reaction from the carbene complex to the alkyl could then be studied.

A new synthetic methodology was developed for the synthesis of (carbonyl)(h^5-cyclopentadienyl)(1-methoxy)ruthenacyclopentene. This series of reactions represents a new approach to the preparation of these types of carbene complexes.

The carbene migratory insertion reaction was studied using PPh_3 and CO to trap the sixteen electron alkyl intermediate formed by the rearrangement. These experiments indicated that under the same conditions in which the iron analog was shown to rearrange the ruthenium compound was unreactive. Labeling the carbene complex with deuterium and following the reaction in situ by NMR spectroscopy confirmed these results. An minimum activation energy of 32 kcal/mol was calculated for the migratory insertion reaction with the ruthenium carbene complex. This compares to a 20 kcal/mol activation barrier for the analogous iron complex. The differences in the energies for these reactions can be attributed to the respective M=C double bonds strengths. Going from iron to ruthenium, the bond strength has increased, therefore, the energy requirements for rearrangement to occur are more demanding.

With this in mind it was hoped we could observe the same trend by looking at carbene complexes with metal centers from the third row of the periodic table. Applying the new synthetic methodology to the preparation of (dicarbonyl)(h^5-cyclopentadienyl)(1-methoxy)tungstacyclopentene was not successful due to unexpected side reactions. Although the preparation of the carbene complex was not successful useful information was obtained concerning the limitations of the synthesis which will be helpful in selecting the appropriate metal ligand systems in future.

CHAPTER 1
INTRODUCTION

Background

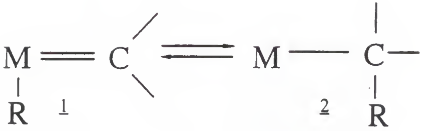


Figure 1

Organometallic carbene chemistry has become an area of intense research in the last few years. Although carbene complexes of various types have been known for several decades, their increased use in C-C and C-H bond forming reactions has made their synthesis and reactivity central to the study of many chemical transformations.[1] Of particular interest are alpha elimination reactions and carbene migratory insertions at metal centers, specifically, the 1,2 migration reaction of alkyls to and from metal centers in organometallic carbene complexes as shown in Figure 1. It

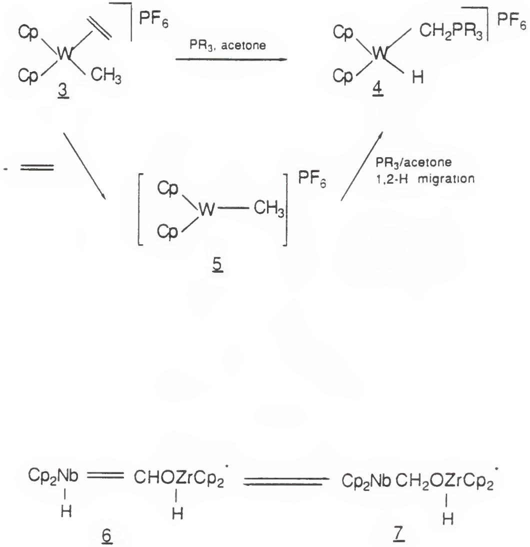

Cp
Cp
W
CH3
PF6
3
PR3, acetone
Cp
Cp
W
CH2PR3
H
PF6
4
Cp
Cp
W
CH3
PF6
5
PR3/acetone
1,2-H migration
Cp2Nb
H
CHOZrCp2
H
6
Cp2Nb CH2OZrCp2
H
7

Figure 2

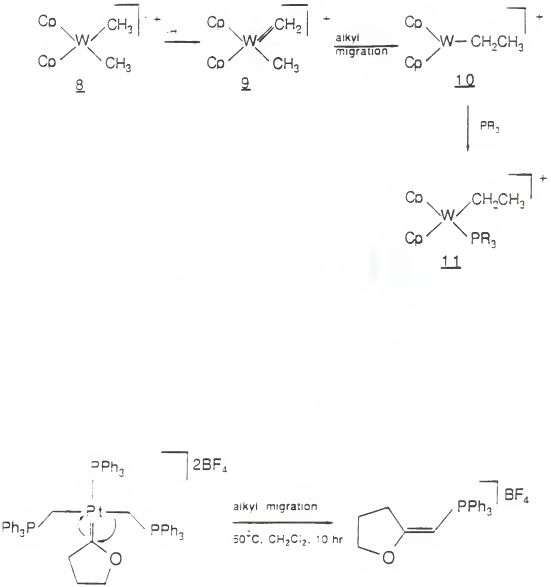

Cp
W
CH3
CH3
8
9
CH2
alkyl migration
W— CH2CH3
10
PR3
11
CH2CH3
PR3
PPh3
2BF4
Ph3P
Pt
PPh3
O
12
alkyl migration
50°C, CH2Cl2, 10 hr
PPh3
BF4
O
13

Figure 3

is interesting to note that the reaction shown in Figure 1 is known in both directions when R is a hydrogen.[2] Some examples of this reaction are shown in Figure 2. In some systems these reactions were shown to be reversible, facile in both directions. When R is an alkyl, however, the reaction is only known in the forward direction, from the carbene complex to the alkyl complex.[3] Examples of this reaction are shown in Figure 3. As this apparent inconsistency became evident, other workers began to investigate the migratory insertion reaction using theory. Hoffman found, for example, through EHMO calculations, the barrier for the forward reaction in Figure 4 (the migration of an alkyl to form a carbene complex) to be only 4 kcal/mol higher in energy than the reverse reaction.[4] This prediction led him and others to believe that the equilibrium in the case of the alkyl should be facile. The energy difference between the alkyl and the carbene complex was also calculated as being small, only 2 kcal/mol. Ziegler and coworkers carried out calculations and studied the migration of hydride in the same system and found, as experiment has shown, that the migration is facile in both directions. The migration of the alkyl from the alkyl complex to the carbene, however, was calculated as being more endothermic and they claim that calculations predict that the migration in the case of the alkyl will only occur

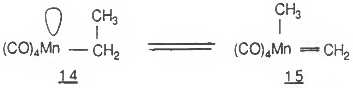


Figure 4

under "forcing conditions."[5] As Cooper and Green had suggested, the bias in these equilibrium reactions was thermodynamic in origin.[6]

One of the most extensive theoretical studies of the alkyl migration reaction was reported by Goddard and coworkers.[7] As shown in Figure 5, they were interested in designing a system which would be representative of the alkyl migration reactions believed to occur in Fischer-Tropsch chemistry.[8] Although it is a general model, limited by the abilities of ab initio calculations to deal with large and complicated systems, it was designed as a representation of the applications of this reaction in the literature. Their conclusions showed that methyl migration has a higher energy barrier than hydride migration partly because of the reorientation required of the sp^3 orbital on

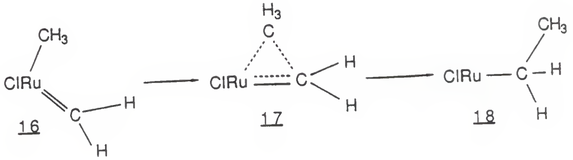


Figure 5

the alkyl carbon for rearrangement to occur. Since the hydride orbital is spherical, this perturbation is absent.

It has not been until very recently that indirect and direct evidence for the 1,2 migration of an alkyl group to a carbene center (an alpha elimination) has been shown. Grubbs and coworkers were examining the decomposition of a Ni alkyl complex and were able to prove, through the use of deuterium labeling studies, the intermediacy of compound 20, as shown in Figure 6.[9] Although the carbene complex was never isolated nor observed spectroscopically, this was the first evidence for the migration of an alkyl group from an alpha-carbon to a carbene complex.

Despite the lack of direct evidence for this rearrangement, the 1,2 alkyl migration reaction had been postulated to occur in various organometallic transformations such as hydrocarbon rearrangements and metal alkyl decompositions.[10] In heterogeneous Fischer-Tropsch catalysis, alkane, alkenes, and other organic fragments and polymers are prepared as CO and H_2 gases are passed over a metal surface. In the most popular model, the CO and H_2 species initially form carbenic fragments on the surface of the catalyst. Alkyl and hydride units are formed on the surface in close proximity and subsequent insertions of carbene fragments into metal carbon and metal hydride bonds

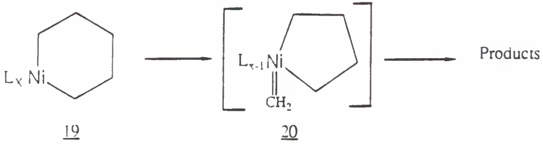


Figure 6

are thought to proceed through the migratory insertion as shown in Figure 7.[8] Studies of the surfaces of these

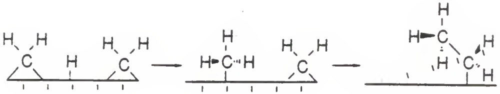


Figure 7

materials have shown the presence of carbenic moieties, and the subsequent involvement of the 1,2 migration reaction of alkyl groups has been proposed as the primary chain lengthening step in the formation of the products. To mimic the carbenic systems many metallic and bimetallic models have been prepared in order to study these reactions in detail.[11]

Given the chemistry just described and its importance in the aforementioned organometallic transformations we decided to focus our attention on the carbene migratory insertion into metal alkyl bonds in order to understand the factors which may be involved in making examples of the reactions rare. In considering the migratory insertion reaction shown in Figure 1, it has been postulated by Cooper and Green that the bias of the equilibrium lies most heavily on the side of the metal alkyl because of the relative C-C versus M-C bond strengths.[5]

In order to study these reactions, we needed to design a system which, by its very nature, would be able to overcome these energy differences. This began our group's investigation into the thermodynamic and electronic requirements of the carbene migratory insertion reaction in metal alkyl complexes. The following discussion is a summary of what we now know about this chemistry, how it is affected by the structure and components of the reaction, and to what extent the requirements of the migration are general to metal complexes through the periodic table.

Current Research

One of the most thoroughly studied systems for the 1,2 alkyl migration reaction in our group is that shown in Figure 8.[12] This is one of the first examples of migration of an alkyl group to give a carbene complex where direct evidence was obtained through the isolation of the carbene complex.[13] Lisko and Jones initially pioneered this work studying the system shown in Figure 9. Both 22 and 29 were prepared in situ by the photolytic decarbonylation of their respective acyl complexes 21 and 28. This has been a convenient method of generating many of the metal alkyl complexes we have studied that could not be prepared directly. The sixteen electron intermediates 23 and 30 are then generated by thermally or photolytically induced

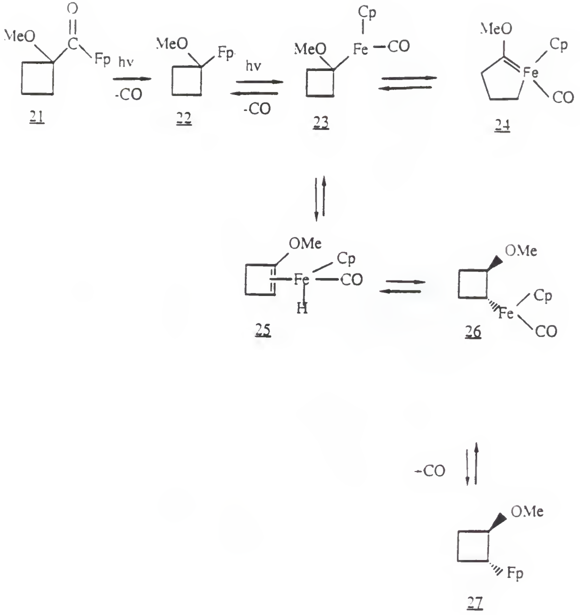

MeO
O
C
Fp
hν
-CO
21
MeO
Fp
22
hν
-CO
Cp
MeO
Fe
CO
23
MeO
Cp
Fe
CO
24
OMe
Cp
Fe
CO
H
25
OMe
Cp
Fe
CO
26
-CO
OMe
Fp
27

Figure 8

dissociative loss of another mole of CO. The sixteen electron intermediates then rearrange to the carbene complexes and the reactions are complete. The origin of the success of this rearrangement is clear. Firstly, one notices that upon migration, the ring sizes have increased by one unit. This change is very significant. The ring strain relief which has been generated has provided a significant amount of energy into this migration in favor of the carbene complex (approximately 20-25 kcal/mol).[14] Stenstrom and Jones studied the migration reaction in more detail with respect to ring strain (again starting from the acyl) and found that ring size is a limiting factor in these reactions: the cyclopentyl alkyl 33 was found not to rearrange and no metallocyclohexene was detected.[12] See Figure 10. This makes sense in that the energy released in going from a cyclopentane to a metallocyclohexene, for example, is not significant (approximately 1-2 kcal/mol).[14]

Another interesting feature common to these reactions is that in all cases rearrangement leads to "Fischer type" carbene complexes.[15] Much is known about this type of carbene complex, and their physical structure is well studied. The carbene carbons on these compounds are very electropositive. This can be exemplified by the low field carbon resonance of the carbene carbon at 350-400ppm in the ^{13}C NMR. Stenstrom and Jones also found that the electronic

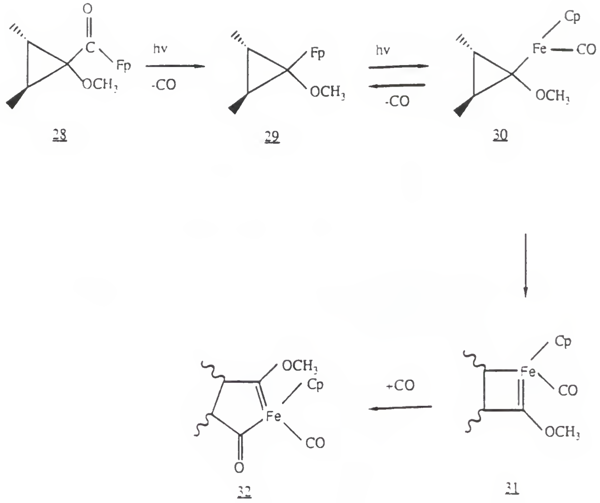

O
C
Fp
OCH$_3$
hv
-CO
28
Fp
OCH$_3$
29
hv
-CO
Cp
Fe
CO
OCH$_3$
30
OCH$_3$
Cp
Fe
CO
O
32
+CO
Cp
Fe
CO
OCH$_3$
31

Figure 9

character of the substituent on the carbene carbon is relevant. In order to stabilize the carbene complex in a favorable manner, the substituent needed to be highly electron donating; success has been found when X is OMe or NR_2 but not when X is H or aryl.[16] (The explanation of this phenomenon can be found when looking at the resonance stabilization of the carbenes as one introduces the alkoxy or amine substituent at the carbene carbon as shown in Figure 11.) In the latter cases no carbene complex was detected. In other words both the ring strain relief and the electronic effects of the substituents have been shown to be significant.

Migration is not the only reaction which occurs once the sixteen electron alkyl intermediate is generated. As shown in Figure 8, a number of side reactions can occur. The reactions shown in Figure 8 are not founded on speculation only. The corresponding aryl-substituted cyclobutyl iron acyl complex was investigated as shown in Figure 12. In this case, ring expansion to give the carbene complex does not occur, instead, decomposition to 46 occurs with beta-hydride elimination as the dominant reaction. (Radical reactions, as an example, were shown not to occur.) Diversion to other products appeared not to be a problem specific to iron. Crowther studied the analogous manganese system shown in Figure 13 and found the same

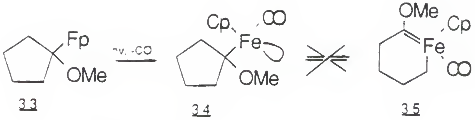
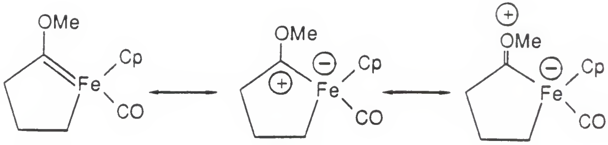


Figure 10

results; beta-hydride elimination was the primary decomposition pathway despite the presence of the methoxy group.[17] It appears then, that the rarity of alkyl migration reactions could also be the result of side reactions which occur faster than the alkyl migration.

Since beta-hydride elimination was the dominant reaction for 58, Crowther tried a alternative cyclic system in which beta-elimination should be retarded; the alpha-methoxybenzocyclobutenyl complex as shown in Figure 14.[18] It was hoped that once the sixteen electron species 68 was generated the benzocyclobutenyl rearrangement would be favored for the following reasons.

Firstly, the strain inherent in the benzocyclobutene ring is approximately 8 kcal/mol higher than the strain



36 37 38

Figure 11

energy of the cyclobutane ring, strain that should be relieved upon rearrangement.[14] Secondly, the methoxy substituent on the alpha carbon would be electronically stabilizing to the "Fischer" carbene complex. Most importantly, however, is that the beta hydride elimination reaction in this system would be unfavorable. The combination of ring strain and antiaromaticity in benzocyclobutadiene will be a significant deterrent to its dissociation from the metal-hydride complex. All of these factors should favor rearrangement relative to beta-hydride elimination. In fact, not only was Crowther able to observe both 1,2 alkyl and aryl migration with the benzocyclobutenyl manganese system, using the analogous ring system for iron, as shown in Figure 15, the yield for the carbene complexes

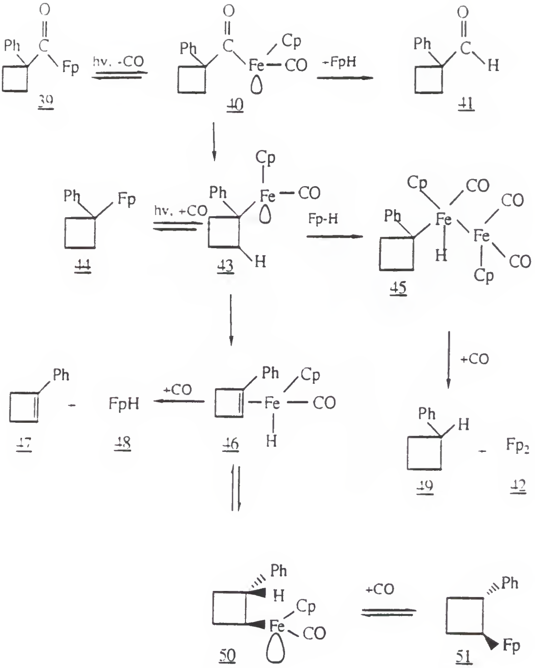

hν, -CO
-FpH
hν, +CO
Fp-H
+CO
+CO
+CO
Fp₂
FpH

Figure 12

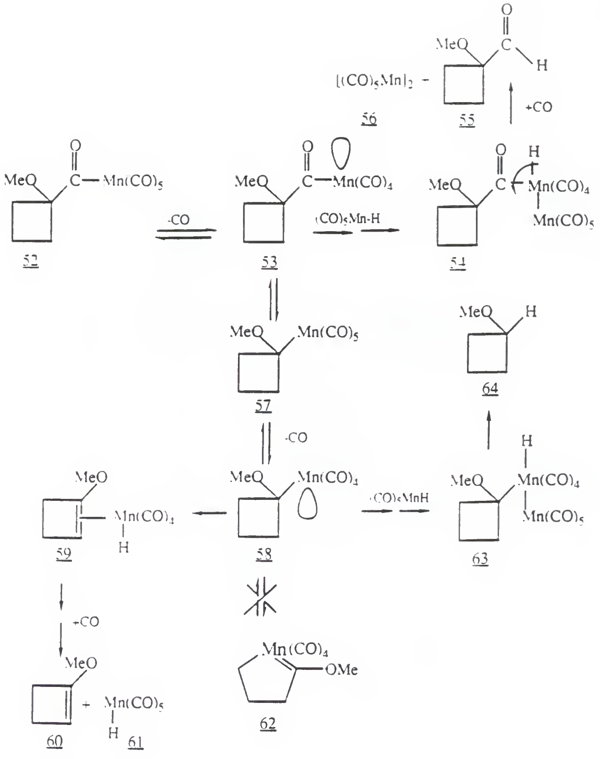

MeO
C
H
[(CO)5Mn]2 +
56
55
+CO
52
-CO
53
(CO)5Mn-H
54
Mn(CO)5
Mn(CO)4
57
-CO
58
59
(CO)5MnH
63
64
+CO
60
61
62
OMe

Figure 13

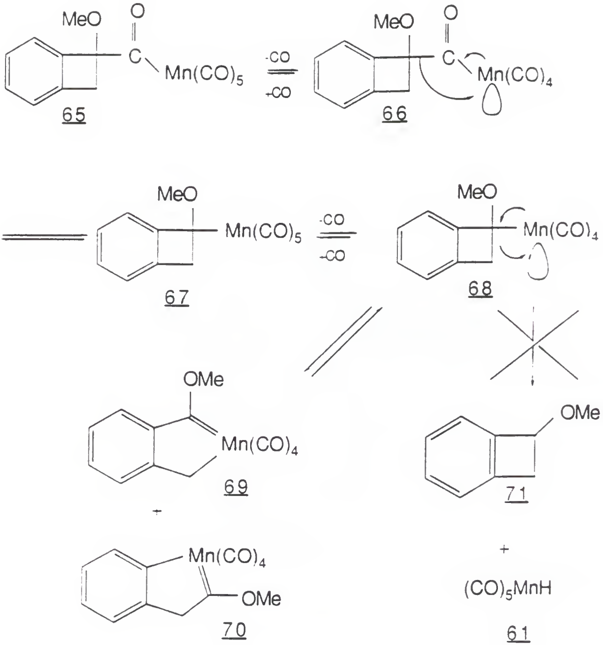

MeO
O
C
Mn(CO)5
65
-CO
+CO
MeO
O
C
Mn(CO)4
66
MeO
Mn(CO)5
67
-CO
-CO
MeO
Mn(CO)4
68
OMe
Mn(CO)4
69
+
Mn(CO)4
OMe
70
OMe
71
+
(CO)5MnH
61

Figure 14

in the benzocyclobutenyl case was as high as 60%, four times that for the cyclobutyl system. Clearly, eliminating side reactions in this chemistry has had a dramatic effect on carbene formation.

Where Do We Go from Here?

In the past, this research group has examined the alkyl migration reaction by altering the character of the cyclic ligands used on some Fe and Mn complexes. Using the knowledge we have gained in the research just described we hoped to use our experience to begin to investigate other metal systems in the periodic table. Fe and Mn are first row metals and it was hoped that we could expand our investigations into metal systems of the second and third rows of the periodic table. In this paper we will examine some Ru, W, and Re complexes. Through these studies we have begun to get a general idea of the effects the metal center itself can have on 1,2 rearrangements of alkyl groups. We will look at the thermodynamics of the previously discussed systems in greater detail and will look at some novel syntheses of the carbene complexes in which we are interested . Finally, we hope to open the door to some new chemistry, propose some alternative strategies in the study of these reactions, and begin to show in a broader sense, how alpha eliminations and carbene migratory insertion

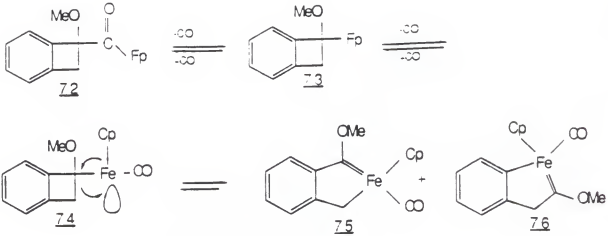


Figure 15

reactions work.

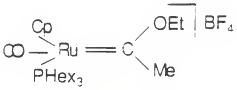
CHAPTER 2
THE CHEMISTRY OF 1-CARBONYL-1-(H^5-CYCLOPENTADIENYL)(2-METHOXY)-1-RUTHENACYCLOPENTENE

Background

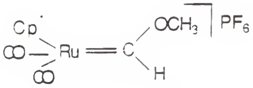
In order to expand our understanding of the migratory insertion reaction just discussed, our objective became to study the generality of these reactions in metal systems other than iron. Because most of the electronic and thermodynamic requirements of the 1,2 alkyl migration were known for iron, we decided to concentrate on a metal of the same group, i.e. ruthenium. There are two major differences between Fe and Ru that can affect the 1,2 alkyl migratory insertion reaction, those being the size and the electronegativity of the second row metal. Because Ru is larger than Fe, the M=C strength is enhanced in the carbene complexes. The filled d orbital on Ru is able to more favorably overlap with the empty p orbital on the carbene carbon. This allows more back donation of electrons from the metal to the carbene carbon, thereby, increasing the M=C bond strength. (These differences can be as high as 20 Kcal/mol between first and second row metals.[18]) If the bond strength can be enhanced, it is hoped that the carbene complex will be stabilized relative to the sixteen electron intermediate and thereby shift the migration equilibrium. Our expectation, then, when comparing the alkyl migration in the Fe and Ru cases is that, the Ru carbene complex should be more stable and the 1,2 alkyl migration reaction from the alkyl to the ruthenium carbene less facile.

Synthesis of Some Ruthenium Acyl complexes

Since we were exploring unknown chemistry in the synthesis of alkyl substituted, cyclic carbene complexes, it was hoped we would find some known model systems for ruthenium. This proved not to be the case. In fact, very few Fischer carbene complexes are known for Ru or for the second row transition metals in general. Most of the systems found for ruthenium are cationic.[19]



77



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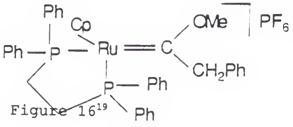

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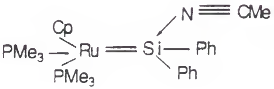


80

Figure 16[19]

Examples of some of these are shown in Figure 16. In view of our success with the iron complexes, we decided to attempt to prepare the desired carbene complexes through the alkyl migration reaction, regardless of the lack of model compounds by previous workers.

Using the synthetic methodology discussed previously, the route chosen for Ru began with the acyl complex. The syntheses and structures of the compounds made are shown in

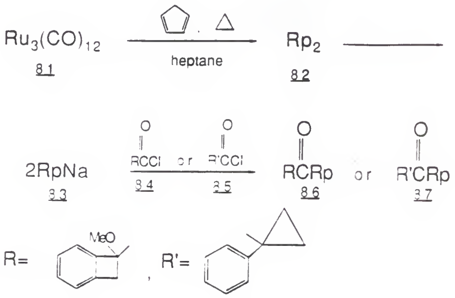


Figure 17

Figure 17. The chemistry is analogous to that used for the iron acyl compounds. (Each acyl complex was prepared in fair to moderate yield.) It was thought, given the success of the benzocyclobutenyl ligand in the Fe and Mn systems,

this would be the most logical ligand for our studies. (See Figures 14 and 15.)

The first step in the generation of the sixteen electron alkyl precursor that could rearrange to the desired carbene complexes 92 and 93, was decarbonylation of 86 as shown in Figure 18. This would produce the sigma complex 90. In situ, the alkyl species should lose another CO ligand and generate the desired sixteen electron complex which should then rearrange to the carbene complexes 92 and 93. Removal of CO ligands from the iron acyl and sigma complexes photochemically is facile. It was found that under the same conditions used in the Fe case however, the ruthenium, benzocyclobutenoyl compound 86 was unreactive (C_6D_6, pyrex tube, 450W Hg lamp). Since it wasn't known if the CO ligand was coming off initially and subsequently recoordinating, the acyl complexes 86 and 87 were photolyzed in the presence of other ligands. These ligands would help to displace the CO from the solvent cage so that recoordination would be inhibited.[20] THF was used as a solvent in these reactions since it is known to weakly coordinate unsaturated metal species. Upon photolysis of 86, however, in the presence of THF no reaction was observed and the starting material was recovered unchanged. To see if difficulty in photochemically inducing decarbonylation of a Rp acyl complex is unique to 86 compound 87 was made,

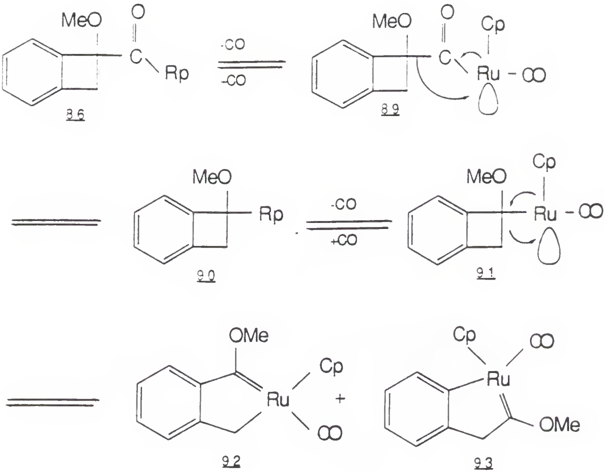


Figure 18

again upon photolysis in C_6D_6, no decarbonylation was observed. When photoinduced decarbonylation of the cyclopropyl phenyl acyl complex 87 was attempted in d6-acetone, also a weakly coordinating solvent, no reaction was found. Dissociation of CO from the cyclopropyl complex 87 photochemically in the presence of $P(Ph)_3$ was also attempted. If the CO were to dissociate, the $P(Ph)_3$ could also coordinate by displacement of the CO from the vicinity of the metal. This would lead to the phosphine substituted acyl species. Phosphine ligands can often be removed thermally more readily than CO, and this might then allow us to generate the desired sixteen electron alkyl precursor via a thermal route.[21] See Figure 19. This, however, did not occur. Photolysis of 87 in the presence of PPh_3 showed no reaction. All of these experiments led to the conclusion that the CO ligands were not coming off the metal center in the Rp complexes. It is interesting to note the lack of information in the literature concerning the photoreactivity of $CpRu(CO)_2$ acyl complexes; not one example of photo or thermally induced decarbonylation of an Rp complex could be found. It was found previously in this group by Lisko that a cycloheptatrienyl acyl complex also could not be decarbonylated photochemically, and alternative routes had to be taken to obtain the desired alkyl complex.[22] Although there is little information on the synthesis and chemistry of ruthenium acyl complexes, the photochemistry of several sigma complexes has been reported. Wrighton and coworkers have shown that with RpR complexes, where R is CH_3 or CH_2CH_3, the primary event upon photolysis is dissociative loss of CO.[23] In these cases, the sixteen electron species were observed directly. (The reactions occurred in isooctane solutions in a pyrex tube, irradiated at 313nm. Wrighton does say that the Ru complexes studied required

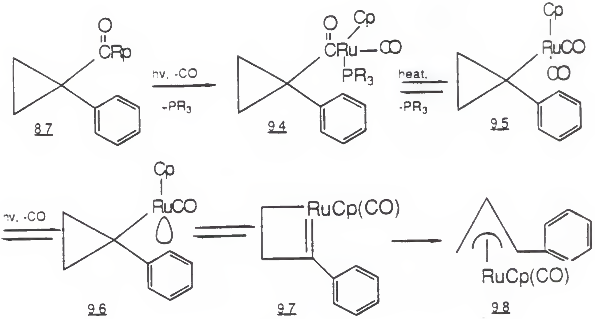


Figure 19

higher energy photolysis than the analogous iron compounds.) Brookhart and coworkers, however, found that the photolysis of RpCH(OMe)Ar gave no CO dissociation, and, again, alternative routes were taken to obtain the desired products.[24] (These reactions were run in benzene with a 450W, quartz lamp.) These results could be explained by the greater size and electron density of the Ru center. More favorable orbital overlap of the ruthenium d orbitals with

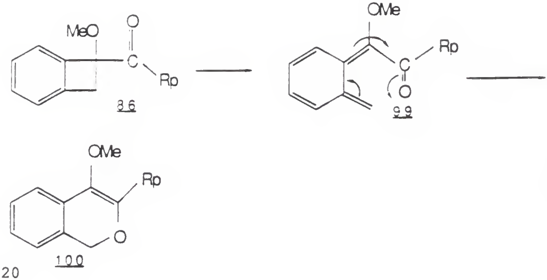


Figure 20

the CO would impart comparatively greater carbon-metal bond strengths for the ruthenium than for the iron complexes. Attempting to use a higher energy wavelength to dissociate the CO's from the metal center, however, created too harsh an environment for 87 (the cyclopropyl phenyl compound 87 was dissolved in hexane and photolyzed using quartz glassware and only decomposition to a complex mixture occurred). Other means of generating the unsaturated species were, therefore, sought.

Chemical decarbonylating methods were also attempted to remove the terminal CO from the metal center. Trimethylamine oxide proved to be a convenient method for Crowther when decarbonylating the benzocyclobutenyl manganese acyl 65.^{25} These conditions could be unfavorable if second decarbonylation occurs to give the carbene because trimethylamine oxide can be reactive towards the carbene complex as it is formed thereby decomposing the final product. In fact when exposing the benzocyclobutenyl ruthenium complex 86 to trimethylamine oxide, complex mixtures of products were formed and the method was abandoned.

Photochemical or chemical decarbonylation are not the only means of removing a CO ligand from a metal center. In the Mn cases discussed in the introduction of this paper, acyl complexes were decarbonylated thermally. Some sigma complexes can also be decarbonylated this way. For example, it has been reported that $CpRu(CO)_2CH_3$ lost CO in the presence of triphenylphospine in refluxing xylene.[26] This method was therefore used to attempt to decarbonylate the 1-methoxycyclobutenyl acyl complex 86. Below 80°C, in C_6D_6, no reaction was observed. However, when 86 was heated in C_6D_6 at 80-85°C for approximately four days a single new product was formed. The material was recrystallized several times from hexane and was found to be a material whose spectra clearly showed that rather than the desired carbene complex the new material has the structure shown in Figure 20. Ring opening of benzocyclobutanes is known to occur under a variety of reaction conditions.[14] In order to attempt a thermal decarbonylation in a system where this kind of ring

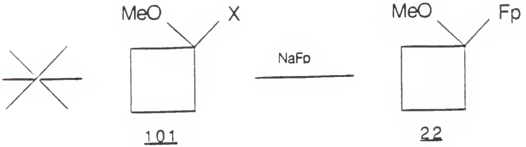


Figure 21

opening was not possible, the cyclopropyl phenyl acyl complex 87 was also heated under the same conditions. It

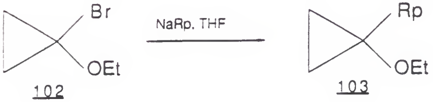


Figure 22

was found to be completely unreactive; no decarbonylation, ring opening, or decomposition occurred. It appeared, then, that the CO ligands on the metal were not thermally labile for these compounds.

For the Ru analogs, we were reluctantly forced to conclude that the preparation of the sixteen electron precursors from the acyl complexes was not a viable option. We therefore attempted to prepare appropriate Rp-alkyl complexes directly by reaction of Rp- with an alpha-halo ether. It was found by Stenstrom that this approach failed for cyclobutyl iron complexes because the required alpha-halo methoxy cyclobutanes were not stable. See Figure 21. On the other hand 1-ethoxy-1-bromocyclopropane is stable and reacts with Fp- to give the sigma complex. By analogy, reaction of 1-ethoxy-1-bromocyclopropane with Rp^- would give 103 as shown in Figure 22. Decarbonylation of this compound would give a sixteen electron metal species 104 which could then rearrange to give the cyclopentenonyl carbene complex 106 as shown in Figure 23. Compound 103, however, could not be made as the reaction of 102 with Rp- gave a complex mixture of products.

At this time it seemed the objectives of this study needed to be reevaluated. The original goal in this work was to study the 1,2 alkyl migration reaction (or alpha elimination) for Ru as had been done for Fe. Making the

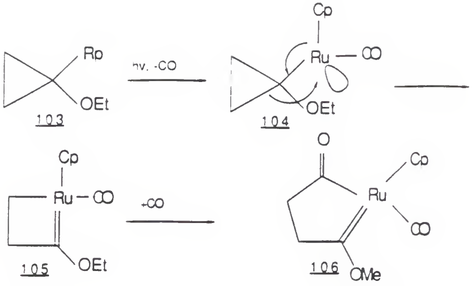
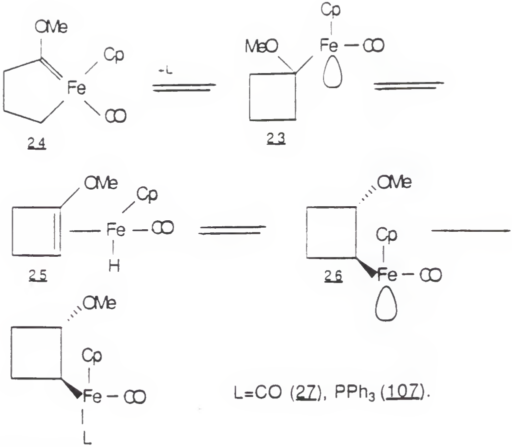


Figure 23

alkyl precursor was only a means of observing this novel rearrangement. For iron it was possible to look at the rearrangement in the forward and reverse directions. Stenstrom, after generating the carbene complex shown in Figure 24, was also able to study the ring contraction step (carbene migratory insertion) in the reaction. Using CO and $P(Ph)_3$ as reagents, upon alkyl migration from the metal to the carbene carbon, the unsaturated, sixteen electron species 26 could be trapped and the new products isolated and characterized. [27] Patton was also able to trap the sixteen electron intermediate with $P(CH_3)_3$. Although the actual product isolated was not the alpha substituted compound, known rearrangement chemistry to the beta substituted complex was observed.



L=CO (27), PPh_3 (107).

Figure 24

Patton was not only able to observe the migration reaction of the carbene complex 24 to the alkyl complex 109, but he was also able to follow the subsequent ring expansion step back to the carbene complex. These reactions were followed by using deuterium labeling experiments as shown in Figure 25. These experiments will be discussed in more detail in later sections of this work. For now, this chemistry serves to show the versatility of having the

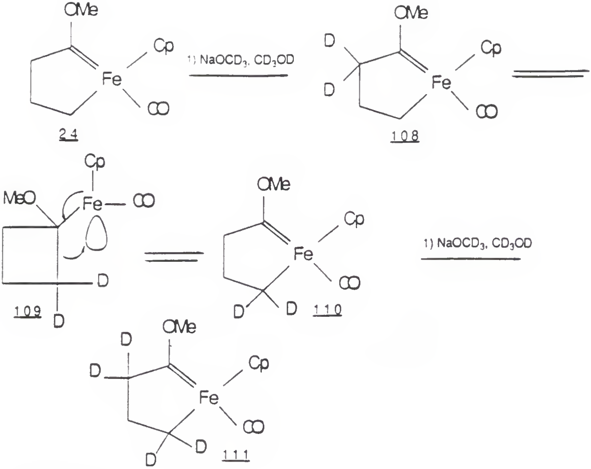


Figure 25

carbene complex in hand.

It has been shown that one can observe the migratory insertion reaction from the carbene complex to the alkyl either using the trapping or deuterium labeling experiments. We needed, then, to take advantage of this chemistry and develop a new synthetic methodology for the preparation of the ruthenium carbene complex. (In this way, it would be possible to compare carbene migratory insertion reactions in

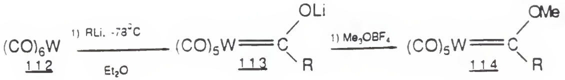


Figure 26

ruthenium systems with their iron analogs.) Synthesis of a cyclic, alkyl substituted carbene complex, however, had not been attempted with the exception of photochemical or thermal decarbonylation reactions from the corresponding acyls. It was important at this point to find a strategy which would be a general procedure for preparing metallocyclopentenes.

Preparation of a Ruthenacyclopentene- the First Stable Ruthenium Carbene Substituted With an Alkyl Group

Our group had never attempted to directly prepare any of the cyclic carbene complexes previously discussed by methods other than through the migration reaction from the corresponding alkyl. The strategy developed for this

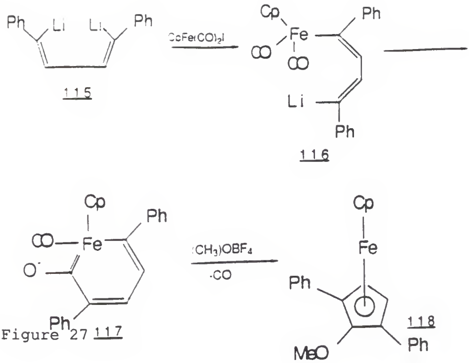


Figure 27

purpose, however, was reminiscent of earlier Fischer carbene chemistry as shown in Figure 26.[12] The difference in the synthesis of the compound of interest to that of the model shown in Figure 26 is that the nucleophile which will attack the terminal carbonyl on the metal would be attached to the metal center. Some work with these types of cyclization reactions have been shown in the literature and were helpful in developing a useful synthesis. (Allison and workers used this methodology to prepare the ferrabenzene 118. Figure 27.[28])

This strategy was first tested on the iron complex 1-carbonyl-1-(h^5-cyclopentadienyl)-2-(methoxy)-1-

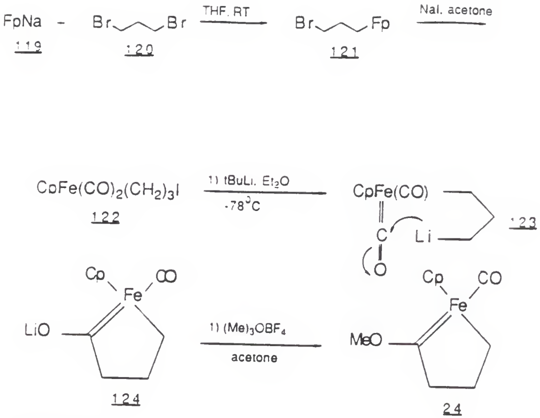


Figure 28

ferracyclopentene 24. Iron is inexpensive and both 121 and 122 were known compounds.[29] It was hoped that the conditions developed for iron would be favorable for the analogous ruthenium compounds.

Sanchez was able to work out the series of reactions shown in Figure 28. Modification of the reported reaction of Fp- with 1,3-dibromopropane was necessary. One of the major side products in this reaction results from

$$\underset{\underline{125}}{MeOSO_2F} + \underset{\underline{126}}{PPh_3Fe(CO)_3C(CO)CH_3Li} \longrightarrow \underset{\underline{127}}{PPh_3Fe(CO)_3C(OMe)CH\underline{3}}$$

$$\underset{\underline{128}}{Me_3OBF_4} + \underset{\underline{129}}{[(CO)_5CrC(O)CH_3Li} \xrightarrow{(H_2O)} \underset{\underline{130}}{(CO)_5CrC(OMe)CH_3}$$

Figure 29

disubstitution of the anion onto the alkane. Adding the anion directly, however, in small quantities to a large excess of 1,3-dibromopropane in THF solved this problem. Lithium exchange with primary halides is limited to alkyl iodides, however, the iodide could not be made directly from reaction of the anion with 1,3-diiodopropane because disubstitution was a significant problem which could not be avoided. The bromide 121 was therefore made first and then converted to the iodide using the known Finklestein reaction.[30]

The most challenging aspect of this synthesis proved to be the lithium exchange reaction of the iodide and subsequent ring closure. The lithium exchange reaction and subsequent ring closure reactions were a "one pot" sequence

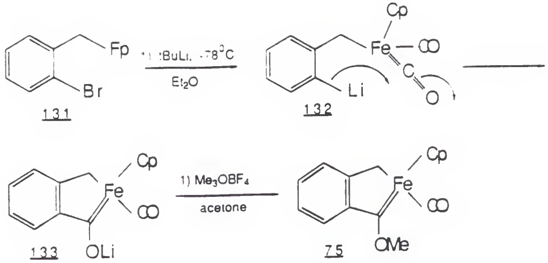


Figure 30

of steps. The conditions of these reactions were optimized by Yang.[31] It was found that the greatest yield of the salt (based on product formation after methylation) was obtained when the addition of t-butyllithium was run at -78°C. Lithium exchange is known to be a facile process at this temperature. The reaction was warmed to -30°C and not allowed to warm further through the subsequent steps including removal of solvent. (The temperature was monitored in the solution of the reaction vessel.) If the reaction was allowed to warm to room temperature, formation of $Fp(CH_2)_3Fp$ was significant. (This side reaction will be discussed in more detail in a subsequent chapter.) The reaction was kept at -30°C for several hours, the solvent was removed, and the residue prepared for the next step of the synthesis; methylation of the lithium salt of the carbene.

Another step which required considerable attention was that of the methylation of the lithium salt of the carbene. Many types of methylating agents can be used, many of which have been successful for other workers in methylating similar types of compounds as shown in Figure 29.[32] The only conditions that were successful for converting 124 to 24, however, were solutions of Me_3OBF_4 in acetone. Other solvent systems typical for these types of reactions were tried but not found successful: in acetone the methylating agent and the substrate are mutually soluble. As can be seen, the yields for the carbene complex using this method relative to photochemical generation of the carbene complex from the acyl, were very high, 60%/32% respectively.

In order to study the generality of the above chemistry we also tried the benzocyclobutenyl system as shown in Figure 30. The reactions were only attempted once and not optimized, but formation of 75, albeit in low yield, was encouraging. The success with this system, however, represented some potential versatility with these reactions. The metal exchange step in this case was done with the aryl bromide as opposed to the aryl iodide since lithium exchange with most aryl halides is facile. The subsequent steps were straight forward, and the carbene complex was

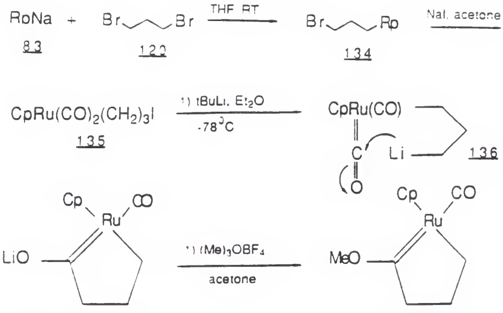


Figure 31

spectroscopically identified.

Having been successful in the synthesis of the cyclopentenyl 24 and benzocyclopentadienyl 75 carbene complex for Fe, we decided to attempt to use this synthesis for ruthenium. In this way we would be able to enter the sought after 1,2 alkyl migration manifold without having to prepare the alkyl complex.

Using the synthetic methodology developed for the iron chemistry, the alkyl bromide and alkyl iodide complexes were prepared for ruthenium as shown in Figure 31. These compounds were not known for ruthenium, however, the yields in these steps were high and the preparation and isolation

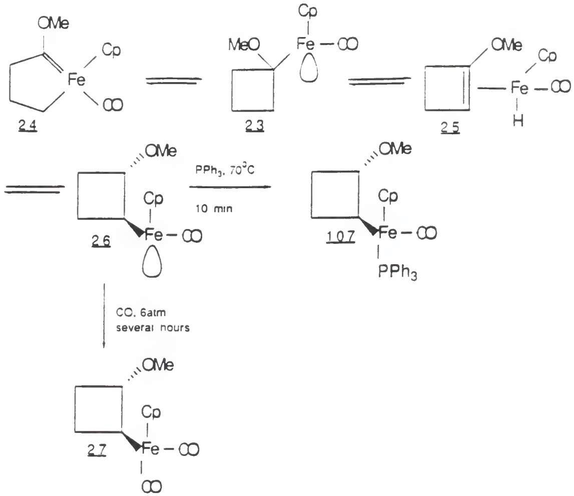
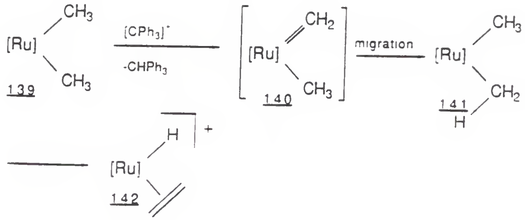


Figure 32

of the compounds straightforward. The subsequent preparation of the carbene complex, however, proved to be quite sensitive to experimental conditions.

The first step in these reactions was the lithium exchange of the alkyl iodide 135. The addition of t-butyl lithium was done at low temperature (-90°C). It was found that if the reactions were run at low concentrations (see experimental), the side products produced could be



$Ru{=}Cp^{\cdot}(PPh_3)Ru.\ Cp^{\cdot}(PmePh_2)Ru$
Model for Fischer-Tropsch Catalysis.

Figure 33

minimized. The side products in the ruthenium chemistry were not straight forward and they were not identified. Maintenance of a low reaction temperature through the addition, however, was advantageous.

The time consuming step in these reactions was the ring closure. Many trials were required to find the appropriate amount of time for its completion. By trial and error, it was found that most side products could be eliminated by simply allowing the reaction to run for 10-12 hours. Apparently, the ring closure for the ruthenium reaction is slower than that for iron. Allowing the reaction temperature to rise to room temperature did not inccrease the formation of $Rp(CH_2)_3Rp$ in these cases. The lithium salt of the final ring closed product was also extremely sensitive to water and air, therefore, extreme precautions were taken in drying and degassing the ether and acetone. All reactions were also carried out under an argon atmosphere.

Methylation did not seem to cause any problems in this synthesis. The reagents were added at -78^0C, and subsequently the mixture was warmed to room temperature. The carbene complex was purified by column chromatography on neutral alumina (activity III) or silica gel and obtained pure as a bright yellow oil(20-25%).

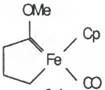
Physical Characteristics of the Ruthenium Carbene

It was noted that one of the first differences between the iron and ruthenium materials were their physical appearance. The iron carbene complex being a dark red oil-like solid and the ruthenium complex being a bright yellow-orange oil. The ^1H and ^{13}C NMR resonances are shown in

Tables I-IV. Some of the more interesting aspects of the spectra of these compounds is the differences in the resonances of the protons and carbons which are close to the metal center. The Cp and alkyl proton peaks in the iron case appear at much higher field than those in the ruthenium carbene complex. This is a reflection of the greater electronegativity of the iron and its effect on the protons in its vicinity. It is also interesting to note that the alkyl protons of the ring in the ruthenium complex are spread out over a greater range and can be integrated very accurately. Unfortunately, the spectra are very complex in that the protons at each position appear to couple to all the protons in the ring system. This was evident by 2D and Spin Decoupled NMR studies. We were not, in either experiment, able to conclusively identify each resonanceinthe ruthenium carbene spectra. The iron case was more complex. The carbon spectra, however, reflects another inherent difference between the metal centers. As can be seen in the chemical shifts of the carbons which are directly attached to the metal center, those peaks in the ruthenium spectrum are much more shielded than those of the iron. Each resonance appears at lower field from the analogous carbon peaks in the iron case. This is a reflection of the electronegativity of the metal centers. The ruthenium center is much less electronegative since it

Table I-IV: ^{1}H and ^{13}C Resonance Data in C_6D_6.

A.



24

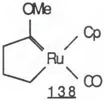
^{1}H NMR*

Peaks	Positions / ppm
Cp	4.26
OMe	3.67
CH_2	1.60-2.60

^{13}C NMR*

Peaks	Positions / ppm
C=M	344.28
CO	222.64
Cp	84.92
OMe	64.36
CH_2	60.17
CH_2	30.05
CH_2	13.58

B.



138

^{1}H NMR*

Peaks	Positions / ppm
Cp	4.73
OMe	3.75
CH_2	1.87-2.80

^{13}C NMR*

Peaks	Positions / ppm
C=M	325.02
CO	207.92
Cp	86.89
OMe	66.53
CH_2	60.13
CH_2	31.39
CH_2	7.65

*=solvent, C_6D_6.

is a second row metal, and it will shield the atoms in its vicinity more effectively than will iron. The carbene, carbonyl, and carbon of the alkyl ring directly attached to the metals most dramatically exemplify this effect.

Besides the respective physical characteristics it is important to note here the actual stability differences between these compounds. The iron compound proved thermally unstable and difficult to handle, in fact, no elemental analysis was obtained as the material would eventually decompose even under rigorously dry and oxygen free conditions. The ruthenium complex is reactive to oxygen, but is very easy to handle at room temperature.

Reactivity

With the cyclopentenyl ruthenium complex in hand, the real focus of our research, the 1,2 alkyl migratory insertion reaction or carbene migratory insertion reaction needed to be addressed. It is possible to study this rearrangement using various methods and we have examined the migration in some iron carbene complexes both from the alkyl to the carbene and also from the carbene back to the alkyl.[12] The reaction we are interested in is the migration reaction from the newly prepared ruthenium carbene complex 138 to the alkyl, 143. The problem here is that rearrangement produces a new sixteen electron, unsaturated complex, which can not be directly observed. Strenstrom had studied the migratory insertion reaction from the cyclopentenyl iron carbene complex to the alkyl using ligand traps such as $P(Ph)_3$ and CO as shown in Figure 32. It is very common in studying transient sixteen electron species in organometallic chemistry to use ligands such as phosphines, CO, nitriles, and coordinating solvents in order to trap unsaturated species in solution.[20,21] These traps would be able to react with the sixteen electron intermediates and, thereby, form detectable and isolable species. It is interesting to note that the isolated compounds in the case of the reactions of CO and $P(Ph)_3$ with 24 were the beta methoxy substituted, 27 and 107, not the alpha substituted sigma complexes. It seems that beta hydride elimination in the sixteen electron species is more facile than the trapping of the sixteen electron complex 23 by the ligand. Once the elimination occurs, however, the entrapment of 26 is facile. These experiments allow one to actually follow the migration reaction as it occurs by monitoring the disappearance of the starting carbene complex and/or the appearance of the sigma complex. Once one has compounds such as 27 and 107, it is also possible to examine the migration reaction from the alkyls to the carbene complex using photochemical or thermal decarbonylation. These experiments have all been done by Stenstrom and clearly indicate the reversibility of the reactions.[12] In

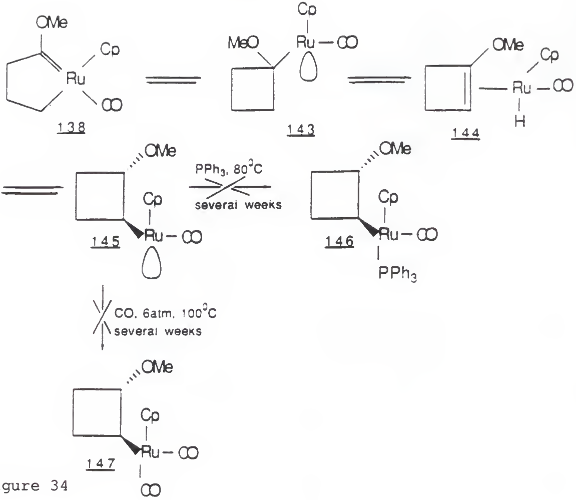


Figure 34

principle, conversion of 24 to 23 could also yield activation parameters for the migratory insertion, and, in fact, maximum values have been obtained. The extraction of the energetics of this migration is extremely important because of the speculation and interest in the applications of this chemistry as a fundamental C-C bond forming reaction in organometallic chemistry.

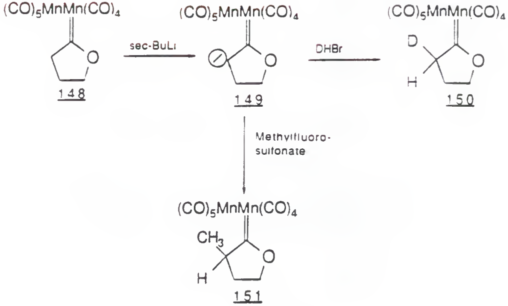


Figure 35

It is interesting when one looks at what is known about the 1,2 migratory insertion reaction in catalysis, particularly Fischer-Tropsch chemistry, to note that ruthenium is often found as a metal center in these processes. See Figure 33. Bi-metallic carbenic centers have been implicated in some catalytic processes and ruthenium compounds have served as good models.[33] Having now synthesized the cyclopentenyl ruthenium carbene complex we were eager to investigate its reactivity. The first question we needed to ask was whether or not the migratory insertion reaction was occurring with 138.

In the iron case, the first test for migratory insertion was the absence of broadening of C-3 or C-5 resonances in the ^{13}C NMR.[12] (These carbons become equivalent upon the ring contraction of 24 to the sixteen electron species. See Figure 25.) This then gave a minimum energy barrier for the contraction of 24 to 23 as 15.1 kcal/mol (63.3 kJ/mol). This barrier is also applicable to the ruthenium carbene complex as no coalesence was observed for the analogous carbons in the NMR.

An upper limit on the contraction of 24 could be obtained by studying its reaction with $P(Ph)_3$. The reaction of 24 with $P(Ph)_3$ was found to give two diastereomers. In these experiments, Strenstrom had found that the phosphine substituted alkyl complex could be formed in approximately ten minutes at 70^{0}C. The carbene was simply put in a NMR tube dissolved in C_6D_6 with 1 equivalent of $P(Ph)_3$. While heating the tube, the reaction could be followed by NMR. The absolute rate of the reaction with one equivalent of $P(Ph)_3$ in C_6D_6 was determined at 50^{0}C by monitoring the Cp resonances. A clean second-order plot was obtained to give a second-order rate constant of $(14.1+0.5)X10^{-3}L/(mol/s)$, corresponding to $G^{+}= 21.6+0.5$ kcal/mol (90.7 kJ mol). For activation parameters, rates were also determined at 30, 54, and 60^{0}C. Arrhenius treatment of the data led to H^{+}= 24.4+1.5kcal/mol and S^{+}= 8+ 2 eu. The same series of experiments were attempted for ruthenium and it was here that we were surprised. At temperatures even as high as 80^{0}C, no reaction was seen with $P(Ph)_3$ after several days as shown in Figure 34. It is possible that the ring contraction step is occurring but one of two things could be happening. The first is that the sixteen electron species is indeed formed at these temperatures, but, for unknown reasons, the phosphine is not trapping the intermediate. This is not likely. Looking at the literature one finds that sixteen electron, cyclopentadienyl, carbonyl, alkyl intermediates for ruthenium behave the same as those for iron. Wrighton has done some extensive studies on the reactivity of some Rp and Fp alkyls upon photodecarbonylation and has found each to react quickly with phosphines.[23] This problem must still be addressed, however, in order to be sure that the cyclic alkyls are behaving as expected. A second possibility is that at the temperatures being worked with here, the phosphine is trapping the sixteen electron intermediate 145, but is dissociating and thereby regenerating 143 which then rearranges back to 138.

If the phosphine is simply not being trapped, one of the possible reasons is because the $P(Ph)_3$ ligand is fairly large. (This doesn't necessarily follow, however, since the analogous iron species substitutes directly and it is a smaller metal center than ruthenium. Still, this difference must be addressed.) To eliminate the influence that the size of the ligand may have on the trapping of the sixteen electron intermediate 145, we looked for alternative means of trapping the reactive complex. The carbene was then exposed to $P(Me)_3$. The size of this phosphine ligand is not only much smaller than the $P(Ph)_3$, but is also a stronger nucleophile.[21] Unfortunately, this reagent decomposed the carbene complex. Other alternatives needed to be explored.

Another means which was used to trap the sixteen electron intermediate of the iron system was CO. This ligand is a common reagent used to coordinate unsaturated metal complexes and being small in size, appeared to be the solution to our problems. Stenstrom dissolved the iron carbene in C_6D_6 in an NMR tube under pressures of 3 and 6 atmospheres of CO. After several hours, in both cases, 27 was isolated as shown in Figure 32.[12] Using the same experimental conditions in the ruthenium case as for iron, however, we again found no reactivity. The ruthenium complex, under 6 atms of CO, showed no reactivity after one month at room temperature. The reaction was then heated, and even at temperatures as high as 100^{0}C, no reaction was observed after 13 days. The carbene complex was very stable and no evidence of any decomposition was observed. (Reaction of 24 with CO was compared directly to those just described. TLC was used to identify the known products of the iron ring contraction.) These results confirm our conclusions from the studies with phosphine and also lessen our suspicion that the sixteen electron species was present but not being trapped because of the size of the ligand used. The reactions were repeated and the carbene complex was found consistently inert. It is worth noting here, however, that CO ligands are known to thermally dissociate from ruthenium alkyl complexes.[26] Again, like the phosphine cases, the temperatures may be too high to give products stable to the reaction conditions.

Although these experiments are consistent with the absence of the ring contraction of the ruthenium complex in these reactions, they do not unequivocably eliminate the possibility of an equilibrium between the carbene complex and the sixteen electron intermediate. It is interesting to note here that we also heated the iron carbene complex in the absence of a ligand to trap the sixteen electron intermediate. What kind of products would be observed if the sixteen electron intermediate is formed and no trapping reagent is present? Would the intermediate ring simply expand back to the more stable carbene complex or would other types of reactions occur. The iron carbene complex 24 was dissolved in C_6D_6 in a sealed NMR tube and heated to 100°C. The carbene complex, after several hours, was observed to have decomposed to various products. The volatile materials were removed under vacuum and found to be primarily 1-methoxycyclobutene and methoxycyclobutane. These products are extremely significant in that they are the products of known chemistry as shown in Figure 12. This tells us that if the sixteen electron species were present in the ruthenium reactions, as it was in the iron case, other evidence would be the decomposition products found through its beta-hydride elimination. None of this chemistry was seen in the ruthenium reactions. It is possible that beta-hydride elimination for iron is faster than for ruthenium. We could also say, however, that the ruthenium sixteen electron species 143 is short lived and we cannot trap it nor observe its chemistry. We now needed to concentrate on a more direct method of looking at the reactivity of the carbene complex.

Patton in our group has done extensive work in studying the ring contraction reaction of the iron complex as shown in Figure 25. The advantage of this chemistry is that the reactions can be followed without depending on the trapping nor the longevity of the sixteen electron intermediate: the molecule is internally marked and all chemistry is followed without outside manipulation. Advantage is taken, in these reactions, of the acidity of the hydrogens on the carbon alpha to the carbene carbon. These hydrogens are known to be very acidic in Fischer carbene complexes. As an example, $(CO)_5Cr{=}C(OMe)\mathbf{CH}_3$ has a $pK_a=8$. The only neutral, substituted methane which exhibits such rapid exchange is nitromethane.[34] Other Fischer carbene complexes have been studied with respect to their acidities such as the example shown in Figure 35. Advantage is taken of the reactivity at this carbon to make these types of carbene complexes useful in organic synthesis.[35] The carbons alpha to the carbene carbon can be functionalized with various electrophiles. In the case of the iron carbene complex upon reaction of 24 with a base such as $NaOCD_3$ in CD_3OD the protons at the alpha carbon are replaced by deuterium. This occurred at −30°C, before the ring contraction was significant. The rearrangement was followed at room temperature by ^1H NMR as the contraction, subsequent ring expansion, and reaction again with base caused the protons at the position next to the metal center to disappear. Following this reaction at various temperatures for iron has given us a more specific value for the activation energy for the ring contraction as 18.98 kcal/mol. Work still needs to be done at refining these experiments. We decided, however, to use these reactions to study the ruthenium system.

The ruthenium carbene complex 138 was reacted with a catalytic amount of $NaOCD_3$ in CD_3OD in a sealed NMR tube. ^1H and ^{13}C NMR as shown in Figure 36 and 37 indicate that both protons on the alkyl chain were replaced by deuterium. In the proton NMR, the multiplet at 2.6 ppm completely disappeared and the multiplet at 2.0 ppm decreased by half. (The ^1H NMR spectra in these cases were taken with a short relaxation time, therefore, the integrations of the Cp resonance is not reliable.) In the ^{13}C NMR the resonance at 61 ppm had also disappeared. The reaction mixture was followed by NMR for two weeks at room temperature and no changes were observed which indicated that rearrangement was occurring. In other words, the alkyl region representing the protons on the alkyl chain remained the same and no changes were observed in the carbon NMR; the resonance of the proton at 2.6 and the carbon next to the carbene carbon (61 ppm) did not grow in, and the resonance of the carbon next to the metal center (7 ppm) did not decrease in intensity. The NMR tube was then heated to 85^0C, and, again, the reaction was monitored. At this point, however, the NMR showed significant changes. After 16 hrs at 85^0C, a new Cp resonance had grown in as had new alkyl proton and carbon resonances. The new material was in no way

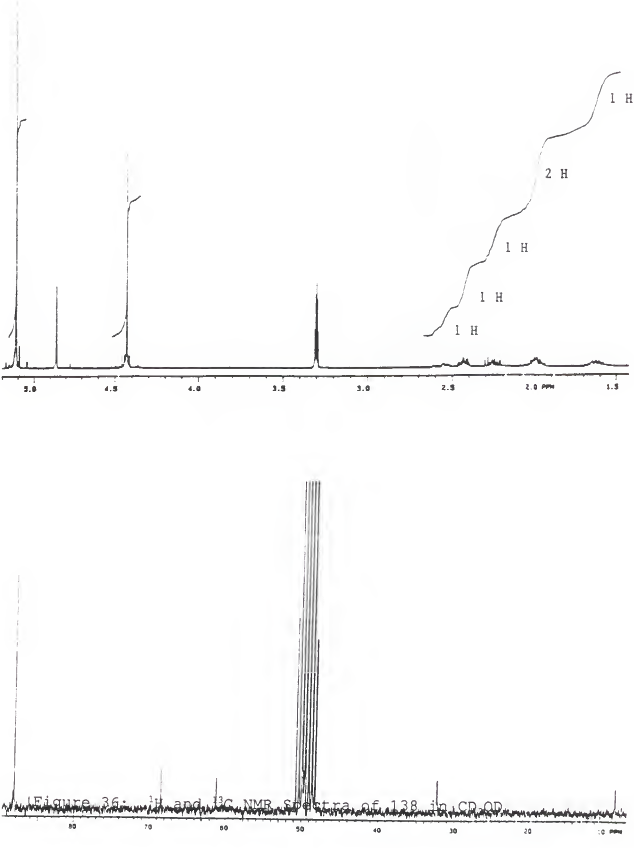


Figure 36: ^1H and ^{13}C NMR Spectra of 138 in CD_3OD

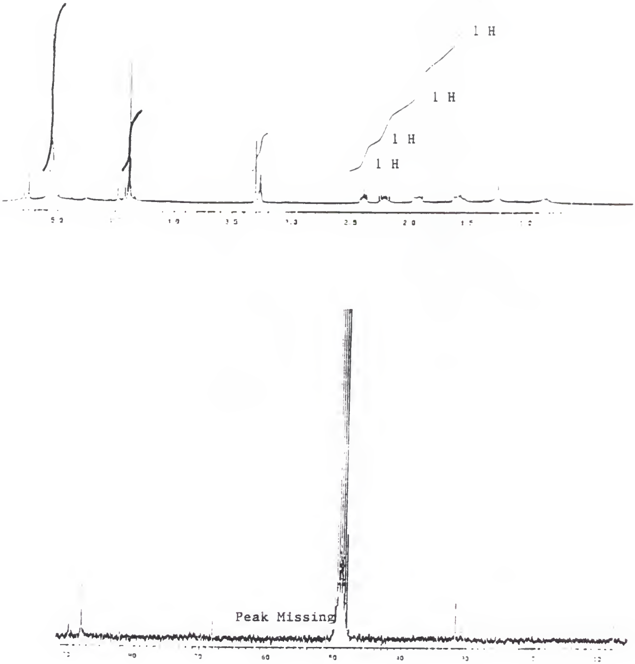


Figure 37: ${}^{1}H$ and ${}^{13}C$ NMR Spectra of 138 After Reaction With $NaOCD_3$.

representative of the di-deuteriosubstituted ruthenium carbene complex. Instead, the carbene had reacted with the $NaOCD_3$ and rearranged in an unknown fashion. No attempts were made to further identify this new compound, but, instead, alternative methods were pursued in finding different conditions for the deuterium exchange reaction.

A reaction that did appear facile with the ruthenium carbene, however, was methoxy exchange with OCD_3. See Figure 38. (The methoxy resonance at 4.4 ppm completely disappeared in the ^1H NMR after three hours at room temperature.) This reaction was also observed with the iron complexes at room temperature but usually occurred over several days. Examples of this kind of reaction are common. Reaction of OR' replacing OR in carbene complexes can be found in many examples such as those shown in Figure 39.[36] The interesting point here, however, is that the exchange reactions for the Ru compound are so fast. The differences in the reactivity of these compounds could simply be a steric one. The ruthenium carbon double bond should be longer than the iron carbon double bond because the Ru metal center is larger and less electronegative. (An example of the increased metal carbon double bond lengths from first to second row metals is evident when comparing the compounds $(CO)_5Cr(OEt)SiPh_3$ and $(CO)_5Mo(OEt)SiPh_3$ with M=C (the metal - carbene bond) lengths of 2.00 and 2.15 A respectively.) The

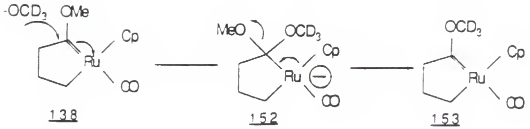


Figure 38

longer Ru=C bond may make it easier for the nucleophile to approach the carbene carbon.

Unfortunately we have not answered the migration question at hand. That is, is the migratory insertion reaction occurring in the ruthenium system under the conditions we have studied? At room temperature, the migration is clearly not occurring, however, at higher temperatures the results are ambiguous because of decomposition. Because of this, we were forced to study the reaction under different reaction conditions.

It was thought that the possible reason for the reaction observed with the $NaOCD_3$ was the nucleophilicity of the base. A solution to this would be to use a strong, non-nucleophilic base such as lithiumdiisopropylamide, quench

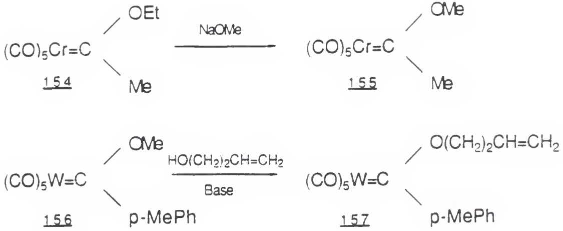


Figure 39

the reaction with deuterium, separate the carbene complex from the reaction mixture, and study the reactions in the absence of base. This would give us the desired substitution without the possibility of the base reacting with the carbene complexes, substituted and non-substituted. The carbene complex 138 was reacted with 6 equivalents of LDA and subsequently quenched with D_2O as shown in Figure 40. The solvent was evaporated, the residue column chromatographed (see experimental), and the pure, deuterium substituted carbene complex 159 was isolated. See Figure 41 and 42. The alkyl region of the ^1H NMR integrated for four protons showing that two protons on the ring had been

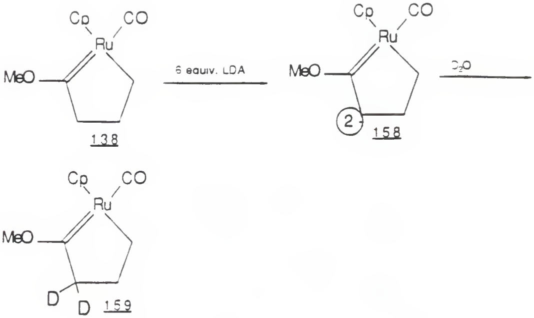


Figure 40

replaced by deuterium. (It should be noted that these proton NMR spectra were taken with relaxation times in excess of 100 seconds. The Cp resonance has a very long relaxation time and T^1 experiments with the carbene complex confirmed it to be 21 seconds.) In this case, both of the protons on the carbon next to the carbene carbon had been substituted. The near absence of the proton resonance at 2.6 ppm and reduction of peak area at 2.0 ppm and a decrease in the carbon resonance at 60.00 ppm in the ^{13}C NMR confirms the replacement. We did not observe a triplet in this case. This would denote mono-substitution of the carbon. It is likely that the pentet representative of di-substitution has been unobservable because of the noise in the spectrum.

The deuterium substitution in this reaction is particularly interesting. In the $NaOCD_3/DOCD_3$ case, the substitution occurs as shown in Figure 43, each proton is removed and the remaining anion immediately quenched by the solvent. In the case of the LDA experiment, however, this type of exchange is not possible. Replacement of the two protons by deuterium can only occur through the dianion. See Figure 40. It is interesting that in the original paper from which the procedure was obtained, the same chemistry was reported for an iron complex as shown in Figure 44.[37] Although some mono-substitution was identified in the reactions with the iron carbene complex, the major product was disubstituted. (In this example the reaction was quenched with MeI instead of D_2O.)

Since it was evident that the protons at the desired position were exchanged for deuterium the migration reaction was then investigated. The carbene complex dissolved in C_6D_6, was sealed in a thick walled NMR tube. The reaction was allowed to stand at room temperature for two days and no reaction or rearrangement was observed. (The reactions were followed by ^1H and ^{13}C NMR.) The mixture was then heated to

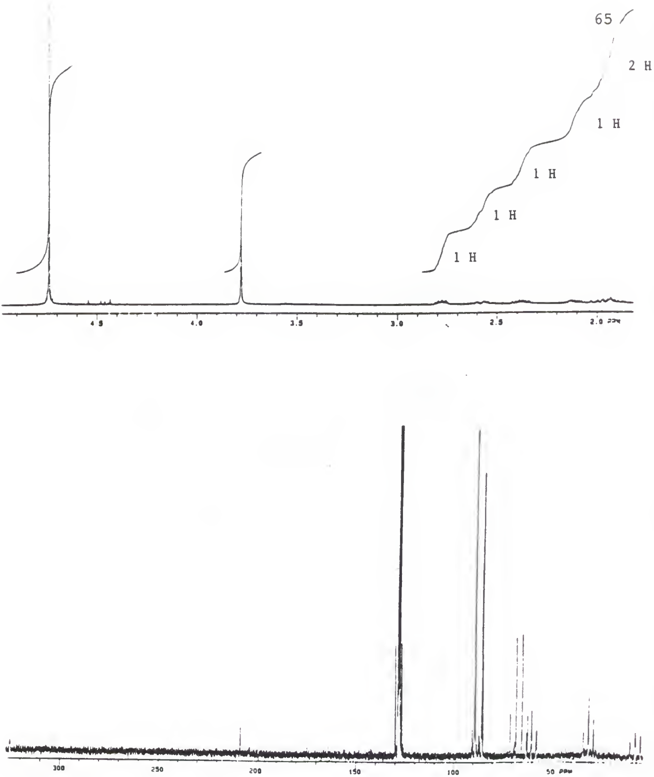


Figure 41: ^1H and ^{13}C NMR Spectra of 138 in C_6D_6.

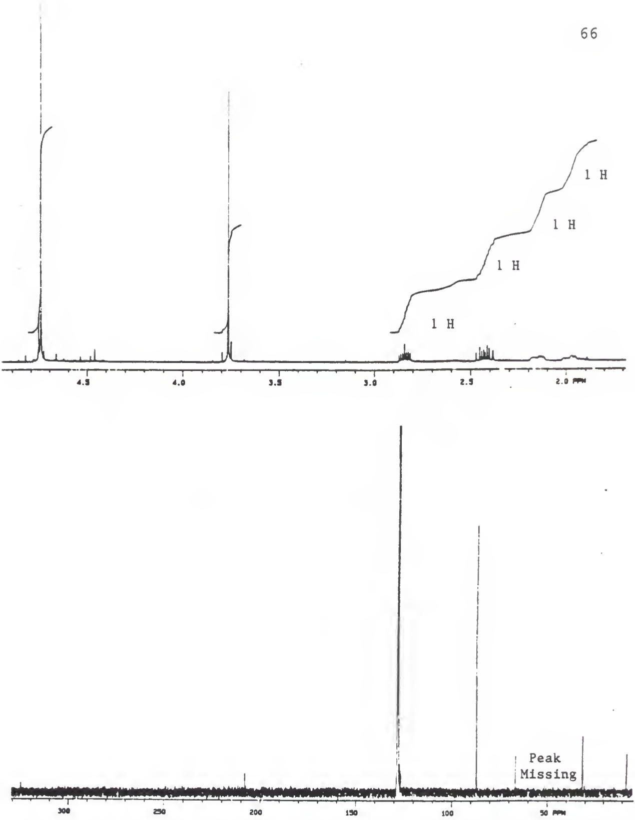


Figure 42: ^1H and ^{13}C NMR Spectra of 138 After Reaction With LDA in C_6D_6.

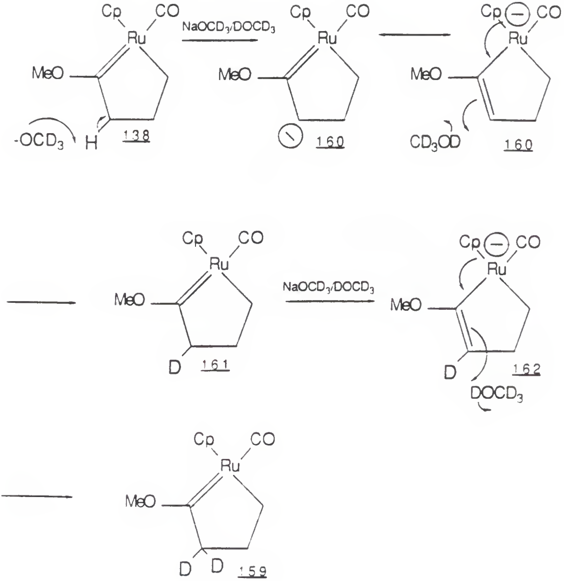

Cp
CO
Ru
MeO
-OCD3
H
138
NaOCD3/DOCD3
160
CD3OD
160
D
161
NaOCD3/DOCD3
D
162
DOCD3
D
D
159

Figure 43

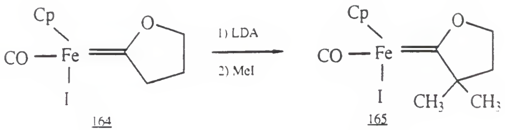
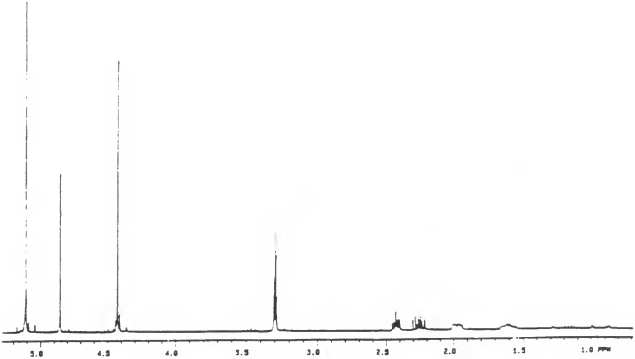


Figure 44

63^{0}C and after four hours no reaction had occurred. Before heating the reaction to higher temperatures the carbene was repurified by column chromatography. (Even small amount of impurities in the high temperature reactions cause decomposition of the carbene complex.)

In order to compare the two carbene complexes we obtained in the LDA and $NaOCD_3$ experiments, the clean carbene complex was then redissolved in CD_3OD and the spectra taken with the proper delay times. Looking at the pattern of the resonances in the alkyl regions of the spectra of the $NaOCD_3$ reactions (Figure 36) and of the LDA reactions (Figure 45) both in CD_3OD, the compounds appear



Fiugre 45: ^{1}H and ^{13}C Spectra of 138 After Reaction With LDA in CD_3OD.

analogous.

The next step in these studies was to increase the temperature in the reactions. The carbene complex was dissolved in C_6D_6 and heated for 24 hours at 100°C, no changes were observed. After 40 hours, however, a new peak appearing at 2.6 ppm began to grow and the peak at 2.0 ppm in the alkyl region was increasing in intensity. ^{13}C NMR showed a triplet at 60 ppm. See Figure 46. This appeared to indicate rearrangement. The conflicting aspect of this data, however, was that none of the proton peaks appeared to be decreasing nor did the peak in the ^{13}C NMR at 7 ppm decrease in intensity. At 56 hours, the peaks at 2.6 and 2.0 ppm continued to grow and there were two sets of peaks at 60 ppm, residual amounts of the triplet and a new singlet. See Figure 47. Again, there was no change in the resonance at 7 ppm. These experiments show that although there is no evidence for the rearrangement in this sample, (the peak at 7 ppm should decrease) an interesting reaction is taking place. Presumably, upon redissolving the carbene sample in C_6D_6, a small amount of water was present. Over time, at high temperature, under the conditions of this experiment, the deuteriums on the carbene complex exchanged with the protons from H_2O. It is interesting that the deuteriums in this position are so acidic. No attempts were made to quantify the rates of the deuterium replacement on the carbon.

Summary

The purpose of the experiments just described was to prepare a metallocyclic carbene complex of ruthenium and attempt to study its migratory insertion reaction to the

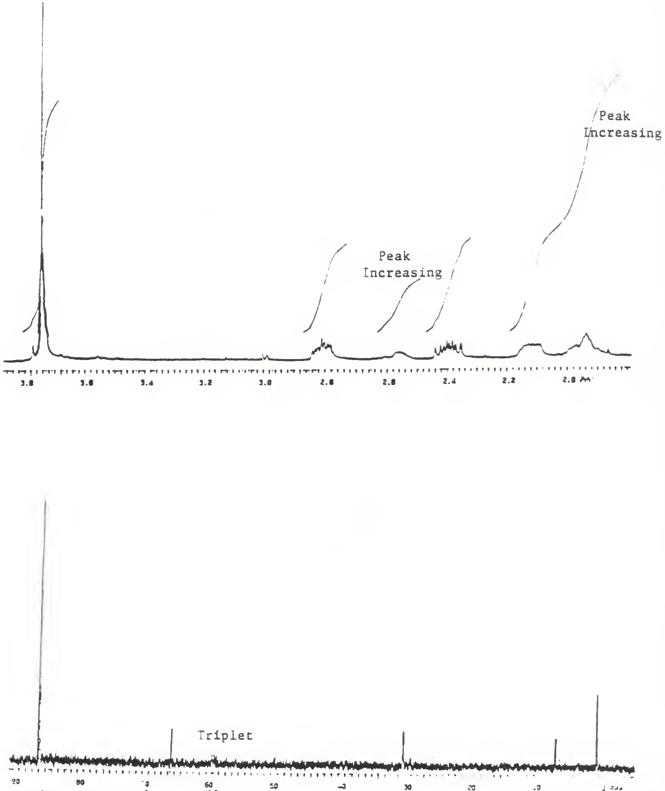


Figure 46: ^{1}H and ^{13}C NMR Spectra of 138 After Reaction With LDA, 40 Hours at 100°C.

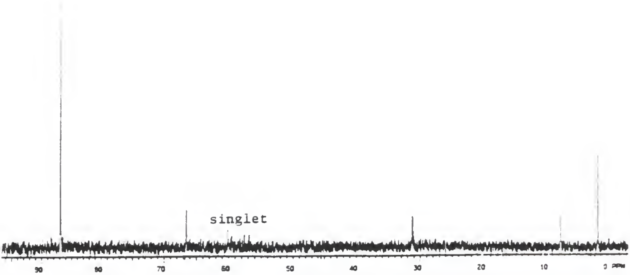


Figure 47: ^{13}C NMR of 155 After 56 Hours at 100^{0}C.

alkyl. The synthesis of 138 was successful and the investigations of its reactivity provided some interesting chemistry. No evidence was obtained which would indicate that the migratory insertion reaction was occurring under the conditions in which the analogous iron carbene complex 24 was known to rearrange. Attempts to trap the sixteen electron intermediate 145 with phosphine and CO were unsuccessful, therefore, the carbene complex 138 was labeled. Because the migration requires high temperature for ruthenium, undesirable side reactions prevented us from seeing rearrangement if it occurred. The LDA reactions, however, allowed us to label the carbene complex and observe its reactivity. Although these reactions were thwarted by the presence of adventitious water, we still have obtained some interesting information about the acidities of the protons next to the carbene carbon.

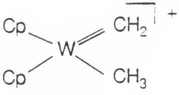
Using the results we have obtained, however, we can begin to assign a minimum energy barrier for the 1,2 migratory insertion reaction for the ruthenium carbene complex. If the ruthenium carbene complex did not rearrange at 100^0C in 40 hours, using this reaction time as the half life of the reaction and assuming a preexpotential of 10^{13}, the minimum activation barrier can be calculated as approximately 32 kcal/mol. Similar calculations on the carbene experiments with CO confirm this value. As was stated earlier in this chapter, Patton had calculated an activation barrier for the analogous iron compound as approximately 19 kcal/mol. The differences in these energies can be attributed to the differences in the respective metal carbon double bonds. In the future it is hoped that a more accurate value can be obtained for the ruthenium reactions. It is interesting, however, that by changing the metal center from the first to the second row, the migration reaction has been affected to such a large magnitude.

CHAPTER 3

ATTEMPTS TO PREPARE A METALLOCYCLOPENTENYL TUNGSTEN CARBENE COMPLEX

Background

In the introduction of this work, the 1,2 alkyl migration reaction shown in Figure 1 was discussed in detail, and in the cases studied the reaction manifold was entered through the preparation of an alkyl complex. Through the rearrangement, the alkyl group (R) migrated from a carbon alpha to a metal center to the metal center with subsequent carbene complex formation. The carbene complexes were shown, in the iron cases, to then undergo the migratory insertion reaction to the alkyl, and these products were trapped and identified. In the ruthenium case, however, the migration reaction could not be studied in this manner since the alkyl precursors could not be prepared. For this reason, a new synthetic methodology was developed for the cyclopentenyl iron and ruthenium carbene complexes 24 and 138 so as to enter the rearrangement manifold from the other direction. In our attempts at observing the 1,2 alkyl migration reaction in second and third row metals of the transition series, we have found that the increased metal carbon bond strengths in the ruthenium carbene complex made



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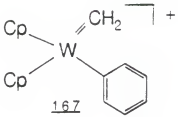

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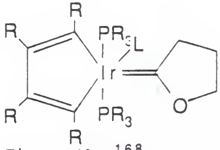

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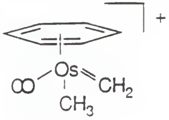

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Figure 48

it less likely to undergo the rearrangement. The carbene complex was also thermally stable and easier to handle as compared to the iron compound.

To continue the study of this trend in increasing carbene complex stability to the alkyl migration reaction, it was decided to begin investigating analogous reactions of metals of the third row of the transition series. In order to do this, tungsten was chosen as the metal center since "Fischer"[5] and other alkyl substituted carbene complexes are well known for tungsten. The model systems shown in Figure 48 are but a few of the many examples of the types of

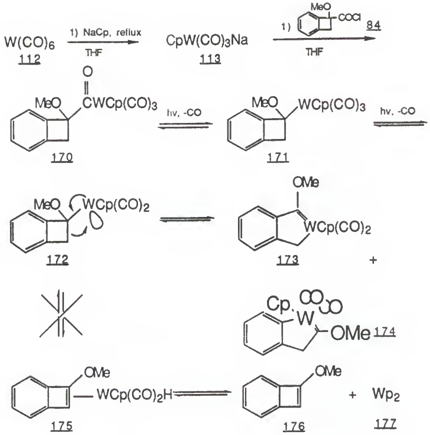


Figure 49

carbene complexes which have characteristics of interest.[38] When studying the alkyl migration reaction it is convenient that the carbene complexes be stable so that the reactions can be investigated in both the forward and reverse directions as shown in Figure 1. It is with this precedence in mind that the following experiments are reported.

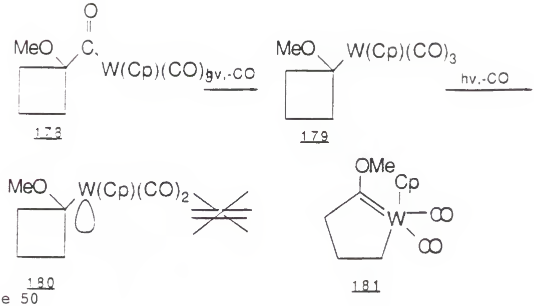


Figure 50

Synthesis of Precursors

Shown in Figure 49 is the approach which was taken to explore the migration reaction. As in the ruthenium case, the acyl complex 170 was the first to be prepared. Crowther had done some work on the methoxy substituted cyclobutyl system as shown in Figure 50 and had not been able to cleanly generate the sigma or carbene complexes from the corresponding acyl.[17] Therefore, the benzocyclobutenyl system appeared to be the most promising; as discussed previously, the benzocyclobutenyl ligand afforded the migration in cases where it was not observed both by favoring rearrangement and by preventing undesirable side reactions, such as 172 to 175.

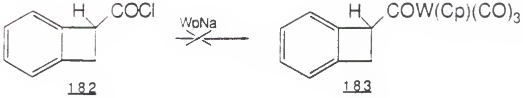


Figure 51

The first step in the study of the CpW(CO)$_3$ system, was to make the methoxy substituted benzocyclobutenyl acyl complex 170. This, however, failed. Attempts to prepare the acyl complex using standard methods, as shown in Figure 49 gave only complex mixtures of products. Problems synthesizing these types of acyl complexes was not new for tungsten. For example, although the methoxy substituted cyclobutyl system had been made, attempts by Crowther to prepare the unsubstituted benzocyclobutenyl tungsten as shown in Figure 51 failed.[39] In the literature one also finds that acyl complexes of the type, CpW(CO)$_3$COR, are extremely rare.[40]

The problem of the preparation of a tungsten complex analogous to 181 was, therefore, attacked from another

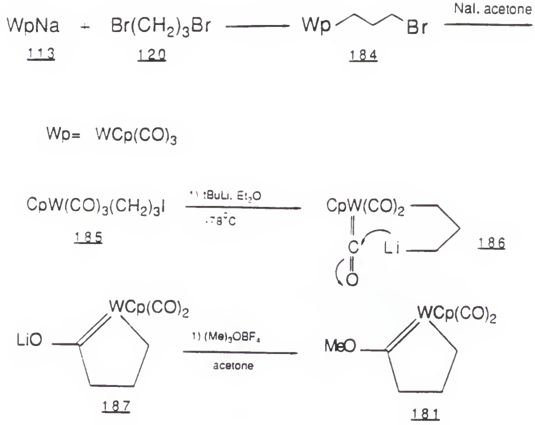


Figure 52

perspective. The previously studied cyclization reaction used with iron and ruthenium was a promising strategy. Using this approach, the carbene complex is made directly and then examined to see if carbene insertion occurs.

Attempted Synthesis of the Carbene Complex.

Figure 52 shows the synthesis of the tungsten alkyls 184 and 185 and the attempted synthesis of the corresponding carbene complex. This approach appeared particularly promising because both 184 and 185 are known compounds, and their syntheses straightforward.[41] Unfortunately, upon reacting 185 with t-butyllithium, subsequent warming, and methylation, the only product obtained from the reaction was $CpW(CO)_3CH_3$. This reaction was quantitative by NMR,

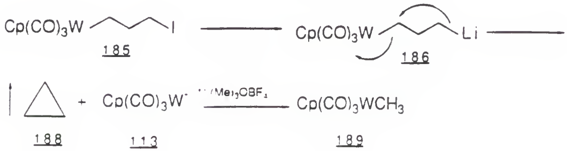


Figure 53

however, after column chromatography, 72% of the $WpCH_3$ was isolated. This result was very surprising. A simple mechanism can be invoked to explain this chemistry, and this is shown in Figure 53. The nucleophilic alkyl lithium simply ring closes on the carbon alpha to the metal on the alkyl chain generating cyclopropane and Wp^-. The Wp^- then

$CpMo(CO)_3(CH_2)_3Br$ + $LM(CO)_nNa$ $\longrightarrow$

190

L=Cp, n=2, M=Fe 119
L=CO, n=4, M=Mn 191

$[L(CO)_nM]_2(CH_2)_3$

L=Cp, n=2, M=Fe 192
L=CO, n=4, M=Mn 193

Figure 54

reacts directly with Me_3OBF_4 and $WpCH_3$ is formed.

Although the concept of this chemistry is simple, precedence for this reaction was not known. Therefore, it was necessary to confirm the accuracy of this proposal. (One example of this type of reaction, where a nucleophile displaces a metal and its ligands, is shown in Figure 54.[42]) The tungsten iodide was reacted with t-Butyllithium at -78°C and the mixture was subsequently warmed to room temperature. The solvent and volatiles were evaporated and collected in a liquid N_2 cooled trap in hopes that the cyclopropane generated in this reaction could be identified. The volatile materials were gas chromatographed and it was indeed found that cyclopropane was present. To the remaining nonvolatile residue dissolved in THF at -78°C was

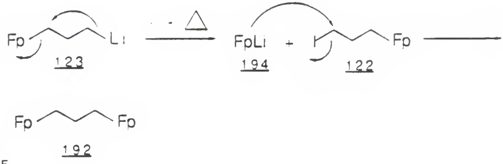


Figure 55

added an excess of CH_3I. The product of this reaction was found to be $WpCH_3$. If the lithiated species were generating cyclopropane as shown in Figure 53, after the cyclopropane was removed, the remaining material should contain Wp−. Reaction with CH_3I and the formation of $WpCH_3$ confirmed that Wp− was a product of these reactions. Wp^- was also independently generated and found to give $WpCH_3$ upon reaction with $(CH_3)_3OBF_4$. It appeared that in the tungsten case, the nucleophilic alkyl lithium was not reacting with the terminal carbonyls on the metal center but with the carbon alpha to the metal center of the alkyl chain. This appeared as an interesting but undesirable side reaction.

Exploring the mechanism of this alternative cyclization reaction with the tungsten system helped explain the existence of some of the side products obtained in the analogous iron chemistry. Besides carbene formation in the iron reactions shown in Figure 28, one of the side products isolated was Fp$(CH_2)_3$Fp. It is possible that this by-product resulted from the reactions shown in Figure 55 where, as in the tungsten example, the alkyl lithium closed on itself with the formation of cyclopropane and Fp−. The Fp−, being fairly reactive, however, was able to generate the observed product by further reaction with Fp$(CH_2)_3$Br.

At this point, the differences between the iron chemistry and the tungsten chemistry require an explanation. It is interesting when looking at the differences in their behavior, one characteristic in these reactions seems to have determined the product distributions; that is, the stabilities of the metal anions themselves. When determining metal anions stabilities it has been common to look at the relative acidities of the corresponding hydrides. These are shown in Table 5.[43] One can see that WpH is much more acidic than FpH or RpH. It is reasonable to correlate this with the chemistry just described. As the stability of the anions increase so too does the cyclization chemistry at the carbons alpha to the metal which generate the corresponding anions and cyclopropane. In the iron case, the Fp− formed is more reactive than is the Wp−, therefore, it may react with residual Fp$(CH_2)_3$I before it has undergone lithium exchange. In the tungsten case, the anion is not reactive enough to compete with the lithium

Table V

Compound	$pK_a^{\bullet}$
$HWCp(CO)_3$	16.1
$HFeCp(CO)_2$	19.4
$HRuCp(CO)_2$	20.2

$^{\bullet}$ = solvent, CH_3CN

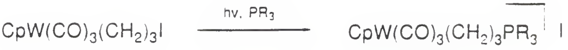
exchange so dimerization does not occur. It is worth noting here, that in the ruthenium reactions no $Rp(CH_2)_3Rp$ or $RpCH_3$ were detected. This result could be a reflection of the relative instability of the Rp- as compared to the stabilities of Fp- and Wp-.

Although this synthetic sequence was not successful for the chosen tungsten case, the chemistry observed here has provided some very important information about the generality of the synthetic methodology. Much of this chemistry could be severely thwarted when using metal ligand systems which possess the potential to produce stable anions. This is a characteristic which must be considered when choosing metal-ligand systems in the future.

Alternative Solutions

Before abandoning this methodology, it was decided to attempt to modify the tungsten metal center with hopes of retarding anion expulsion relative to ring closure. One way we might do this would be to make the $CpW(CO)_3^-$ species a poorer leaving group by putting more electron density onto the metal center. However, it was recognized that this would also reduce the electrophilicity of the carbonyl so it was impossible to predict , a priori, if the desired reaction would be favored.

One common method of adding electron density onto a metal center is accomplished by replacing an electron withdrawing CO with a donor ligand such as a phosphine.[21] The main problem with this strategy, however, was in the synthesis of the phosphine substituted complexes. The most common method used to exchange carbonyl ligands by phosphines is photochemical dissociation of a carbonyl from the metal in the presence of a phosphine. The phosphine ligand is not photochemically labile, therefore, the new phosphine complex is generally stable under the reaction conditions. Unfortunately for the alkyl iodide precursors we were interested in, formation of phosphonium salt was



$$CpW(CO)_3(CH_2)_3I \xrightarrow{h\nu,\ PR_3} \overline{CpW(CO)_3(CH_2)_3PR_3}\ I$$

185 195

Figure 56

faster than CO substitution. (See Figure 56.) A possible way to make phosphine substitution competitive with phosphonium salt formation would be by photolyzing the alkyl complex in the presence of a weakly coordinating solvent which would replace the CO ligand under photolytic conditions. This ligand might then be rapidly displaced thermally by the phosphine. To test the feasibility of this approach, this was attempted first with the $CpW(CO)_3CH_3$ complex using d_3-acetonitrile as the solvent as shown in Figure 57. Acetonitrile is known to be a good two electron donor whose coordination would be weak enough so that it could be displaced by the phosphine.[44] The photolysis of the tungsten methyl complex in CD_3CN, however, resulted in a complex mixture of products.

Another strategy for introducing a phosphine ligand is outlined in Figure 58. In this case, the phosphine is introduced before preparation of the alkyl complex. These

$$\underset{\underline{185}}{\mathrm{CpW(CO)_3(CH_2)_3I}} \xrightarrow[\text{2) acetonitrile}]{\text{1) } h\nu\text{, -CO}} \underset{\underline{196}}{\mathrm{CpW(CO)_2(CH_3CN)(CH_2)_3I}}$$

$$\xrightarrow{\text{1) PR}_3} \underset{\underline{197}}{\mathrm{CpW(CO)_2(PR_3)(CH_2)_3I}}$$

Figure 57

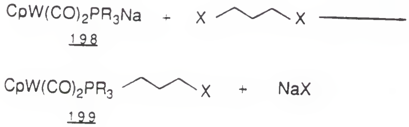


Figure 58

anions appeared difficult to prepare and somewhat rare, therefore, this route was not desirable.[45]

Before attempting to pursue this chemistry further, we decided to test the feasibility of our approach by determining if carbonyl carbons on a simple model tungsten

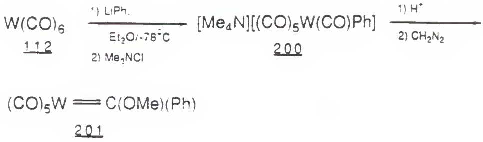


Figure 59

alkyl complex would react with an alkyllithium reagent to give a carbene precursor. It is known that tungsten carbonyl is very reactive with nucleophiles as shown in Figure 59, and carbenes are made after subsequent alkylation of the anions. It was found, however, that $CpW(CO)_3CH_3$ is completely inert to MeLi or PhLi at -78^0C or room temperature (these reactions were followed in situ by IR spectroscopy). In no case was there any sign of reaction of any kind; only starting materials remained even after stirring for several hours. Indeed, the Cp has had a dramatic effect on the reactivity of the carbonyl carbons.

Summary

Although attempts to prepare a cyclic, alkyl substituted carbene complex were unsuccessful for tungsten, our study of the system provided some valuable information about the general problems that might be encountered when using the synthetic methodology developed and shown to be successful for iron and ruthenium. Of special concern are side reactions involving expulsion of the alkyl chain. To succeed with a given metal, ligand systems must be chosen which will provide significant reactivity at the terminal carbonyls and a metal anion that is unstable enough to preclude elimination.

CHAPTER 4
THE ATTEMPTED PREPARATION OF AN ACYCLIC, ALKYL SUBSTITUTED RHENIUM CARBENE COMPLEX

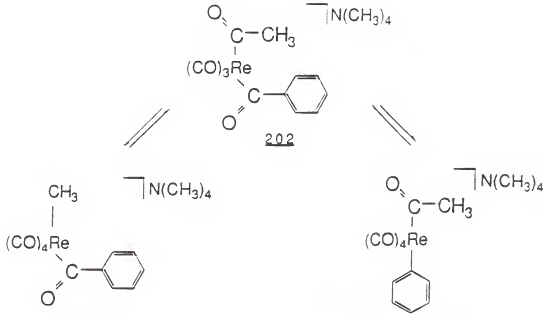
Introduction

The studies presented thus far of the 1,2 alkyl migration reaction have given us some novel information about the electronic and thermodynamic requirements of this reaction. The rearrangement was shown to be sensitive to the structural nature of the migrating group in that ring strain relief was required in order to drive the equilibrium towards the carbene complex. The electronic requirements were also investigated and all of the carbene complexes isolated had electron donating groups on the carbene carbons. Through the ruthenium system, we have also shown that the characteristics of the metal center will affect the 1,2 alkyl migration reaction because of its perturbations of the metal carbon bond strengths. In direct comparison with the metallocyclopentenyl iron carbene complex 24, the analogous ruthenium compound did not rearrange to the alkyl: the ruthenium carbon bond strength biased the equilibrium in favor of the carbene complex. If, then, we were to utilize a larger metal center, such as that from the third row, we could possibly isolate stable alkyl substituted carbene complexes for rearrangement studies which are not cyclic nor heteroatom substituted. The increased contribution of the bond strengths may help to bias the equilibrium so that we can observe the reaction with stable isolated complexes.

The following chapter is a discussion of some preliminary work which has been done in an attempt to study the 1,2 alkyl migration reaction in a system which has rhenium as its metal center. In chapter one, examples of Crowther's work with selected manganese complexes showed that the attempted preparation of the metallocyclopentenyl manganese carbene complex from alkyl precursors was unsuccessful due dominant side reactions. From trends which were observed with the iron and ruthenium cases, the rhenium model was attempted with some modification. Although we have not been successful in isolating the carbne and observing its rearrangement as yet, these results have laid some significant ground work for future work. From this work, it is hoped that future workers will be able to modify our experiments and use the information obtained to successfully study the 1,2 alkyl migration with the first non-cyclic carbene complex.

Background

Carbene complexes of third row transition metals are not difficult to find.[38] As discussed in the previous



202

203

204

Figure 60

chapter, Fischer carbene complexes of tungsten are ubiquitous, and their properties extensively studied. Carbene complexes of iridium are also common and have been shown to be involved in alpha elimination reactions of alkyls as shown in Figure 48.[46] Also, the carbenes in Figure 48 are alkyl substituted, a rare occurrence for the late transition metal carbene complexes.

In an interesting paper in 1980, Casey and coworkers reported investigations of the migratory aptitudes of methyl and phenyl groups in some rhenium carbonyl complexes.[47] See Figure 60. Of particular interest in these studies were

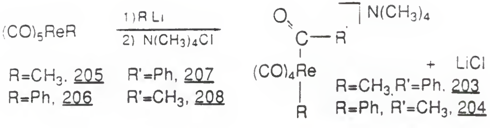


Figure 61

the preparations of the tetramethyl ammonium salts shown in Figure 61 because each acyl complex, upon alkylation would generate a new alkyl-substituted Fischer carbene complex for rhenium as shown in Figure 62. These carbene complexes are of the same basic structure as the cyclopentenyl iron and ruthenium compounds 24 and 138 in that the metal center is alkyl substituted and saturated. The carbene carbon in these cases would also be alkoxy substituted and stabilized. How, then, would these compounds be different from those with which we have become familiar? In these examples, the carbene complexes would be acyclic. For the chemistry discussed in previous sections, the cyclic nature of the alkyl and carbene complexes was a significant factor in the chemistry of the rearrangement. In fact, no examples of

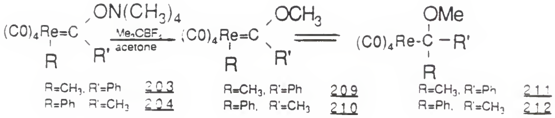
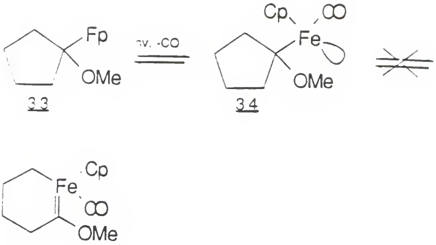


Figure 62

alkyl substituted carbene complexes had been isolated in the iron systems except those of the ring systems of three and four carbons to stabilize the carbene complexes. All attempts to prepare carbene complexes from alpha-eliminations in large ring systems had failed due to a decrease in the magnitude of the driving force for the migration. See Figure 63. It was hoped that we could compensate for the loss of this strain by utilizing the strength of the rhenium-carbon double bonds. The increased bond strengths should push the equilibrium to favor the carbene complex.

Initially, when searching the literature for a precedent for the formation of alkyl substituted Fischer carbene complexes for rhenium, unlike the tungsten and iridium counterparts, we were surprised to find very little information. Although the salts in Figure 60 had been prepared, alkylation of the materials or the preparation of



33 34 35

Figure 63

similar carbene species were not known. Much work has been done by Gladysz and others with Fischer carbene complexes of rhenium with cyclopentadienyl and nitrosyl ligands as shown in Figure 64.[48] These compounds have been studied intensively and have been found to be stable. Other examples of Fischer carbene complexes of rhenium are shown in Figure 65, and although they are bimetallic in nature, their inherent similarities to the compounds in which we were interested were encouraging.[49] Of particular interest were the preparations of these carbenes using methods very similar to those we have become familiar as shown in Figure 66.[50] After nucleophilic attack by LiR on a terminal carbonyl on the rhenium, the intermediate salts of the carbene complexes were subsequently alkylated by several methods. Whether the rhenium carbonyl complexes in which we were specifically interested are likely to be isolable is not clear. Casey, however, was able to prepare the

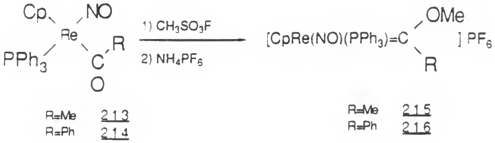


Figure 64

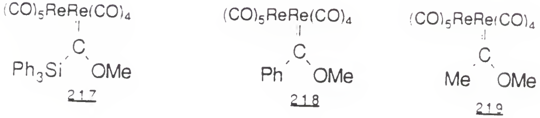


Figure 65

complexes shown in Figure 67. These materials, acyl

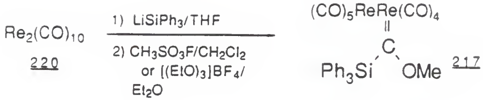


Figure 66

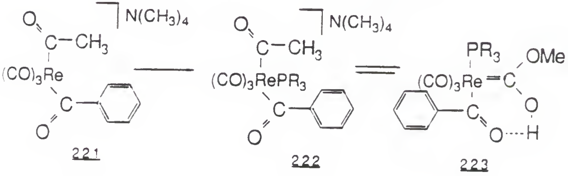


Figure 67

substituted, hydroxy carbene complexes were most analogous to the compounds in which we were interested.

Attempted Preparation of a Rhenium Carbene Complex

The starting materials of interest were made by a modified procedure of Hieber.[51] The synthetic sequence for the preparation of the tetramethyl ammonium salt is shown in Figure 68. The phenyl substituted sigma complex (R=Ph)

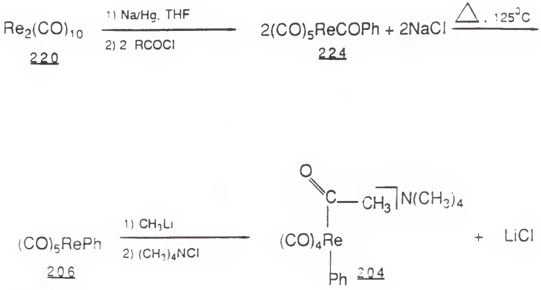


Figure 68

was the focus because the starting materials were easier to handle and purify than the corresponding methyl compound. Although the acyl and sigma complexes 224 and 206 were known materials, their purification proved to be difficult. When the acyl complex was prepared, in most cases, the reaction yielded an oily material which could not be separated from the acyl complex by the sublimation procedures reported in the literature. These side products could be seen in the ^{1}H NMR as a series of very strong multiplets at 2.0, 3.5, and 4.2 ppm. These compound(s) were not identified, but attempts at removing them from the reaction mixture were successful. The oily residue could be sublimed once, to remove the products of the reaction from NaCl. The sublimate was then washed in ether at -78^{0}C. This removed most of the oily impurities leaving pure acyl complex, 224. Decarbonylation of the acyl to the sigma complex was achieved after several successive sublimations at temperatures no higher than 125^{0}C. (Decomposition was rapid at higher temperatures and a brown residue was formed.) The sigma complex was used as a very pure pale yellow solid. Removal of all of the acyl complex or residual $Re_2(CO)_{10}$ from the product was essential for clean reaction with the alkyl lithium reagent. (These compounds also react rapidly with the alkyl lithium reagents.) In cases where residual amounts of the acyl complex or dimer were present, the sigma complex was washed with ether at -78^{0}C and these materials dissolved leaving the sigma complex as a pale yellow solid behind.

The tetramethyl ammonium salt of the carbene complex was prepared by the method of Casey by reaction of the sigma complex with MeLi, extraction of the anion into water, and cation exchange with tetramethyl ammonium chloride. The initially formed lithium salt of the carbene was also isolated and its ^1H and ^{13}C spectra recorded for future reference. Interestingly, although the lithium salts of the ruthenium and iron cyclic carbene complexes previously shown were quite unstable and difficult to handle, the lithium salt of this rhenium carbene complex was fairly sturdy. The salt was stable for several days in benzene. Once these compounds were made and we were confident we could prepare the salt of the carbene, the alkylation step was pursued.

The alkylation chemistry was done with the lithium salt of the carbene so as to avoid the ion exchange in the synthesis. After reaction of 206 with MeLi, the solvent was evaporated and the residue dissolved in d_6-acetone. This was cooled to -78^0C and added to 1 equivalent of Me_3OBF_4. The reaction was then warmed to room temperature and followed by ^1H and ^{13}C NMR. After thirty minutes, the spectra showed rapid reactivity. Figures 69-71 show the progress of the reaction. The phenyl region of the ^1H NMR spectra was useful in following the course of the reaction, and it indicated new products being formed. The ^{13}C NMR spectra were also significant. As the lithium salt of the carbene was disappearing a new lowfield peak was evident (280ppm). The phenyl and alkyl region also showed a new

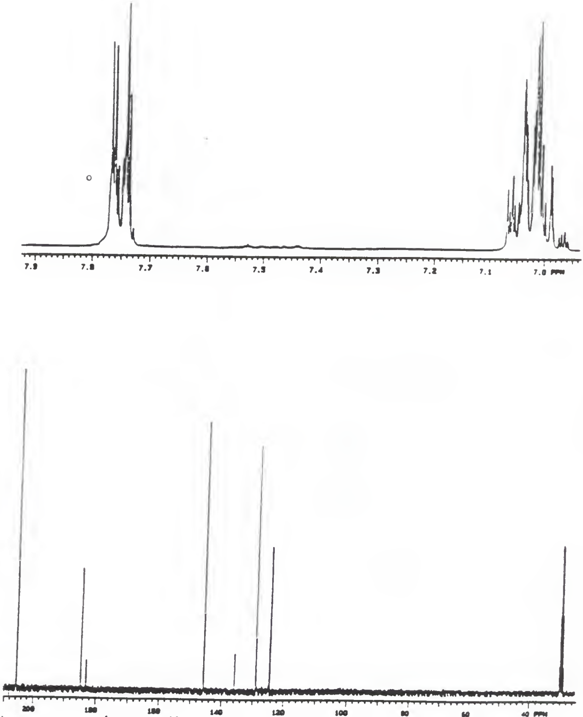


Figure 69: ^1H and ^{13}C Spectra of $PhRe(CO)_5$ in d_6-Acetone.

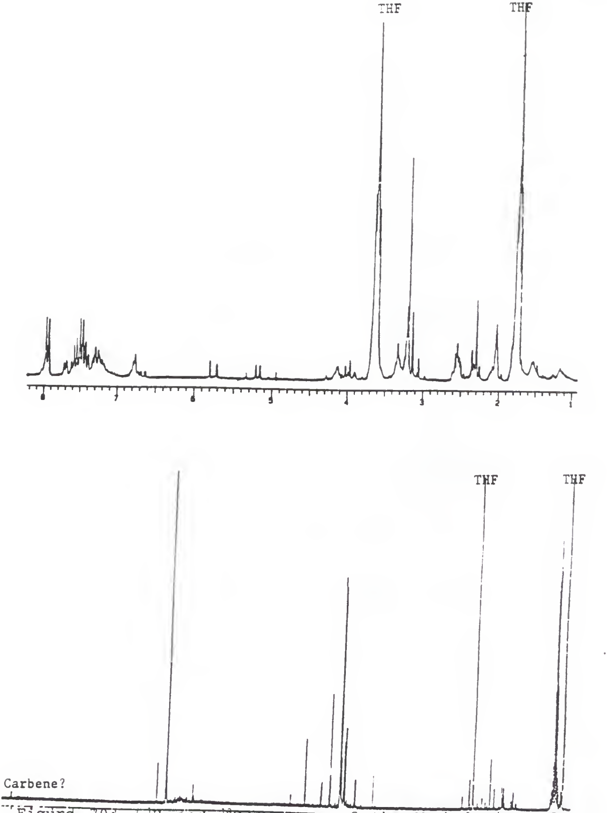


Figure 70: ^{1}H and ^{13}C Spectra of the Methylation of the PhRe(CO)$_5$ After One Half Hour in d_6-Acetone.

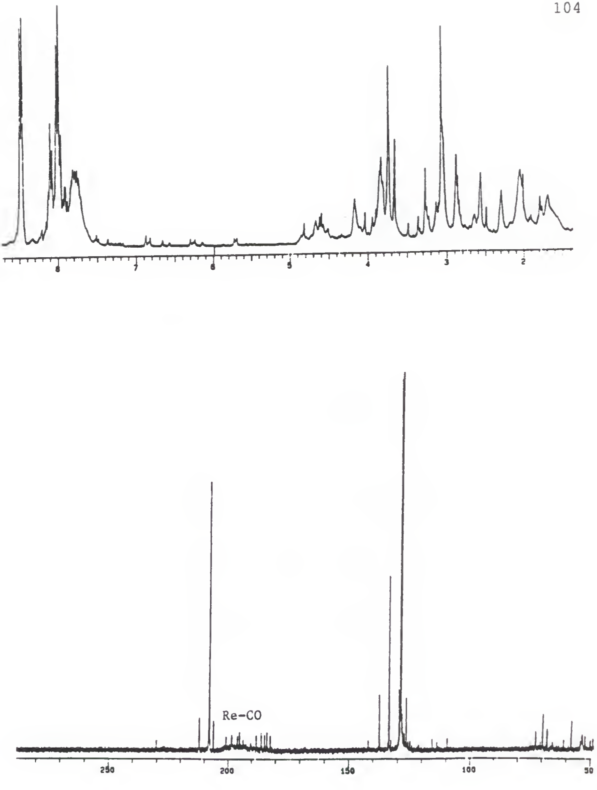


Figure 71: ^1H and ^{13}C Spectra of Methylation of $PhRe(CO)_5$ After Several Hours in d_6-Acetone.

pattern of resonances. As time went on, however, the lowfield resonance disappeared and resonances from new products appeared. After several hours the reaction was complete. Unfortunately, the final product mixtures were very complex and isolation of single materials by column chromatography (silica or alumina), sublimation, or various recrystallization techniques was not successful. The alkylation step was repeated several times and found to give the same intermediates and products. Attempts to isolate the intermediate at low temperature were unsuccessful as decomposition could be observed by NMR at temperatures as low as -30°C. The presence of this intermediate with the resonances at 280 ppm looked promising in that it indicated the presence of the desired carbene complex 210. The next seccion will discuss the investigation of the intermediate and its decomposition.

A Study of the Mechanism of Decomposition

If we assume that the intermediate product from these reactions was indeed the desired carbene complex (the extremely low field resonance suggests this to be very likely)41,42 based on what we know about the chemistry of other alkyl substituted carbene complexes specific reaction products which result from the carbene migratory insertion reaction were, therefore, sought. In other words, it is

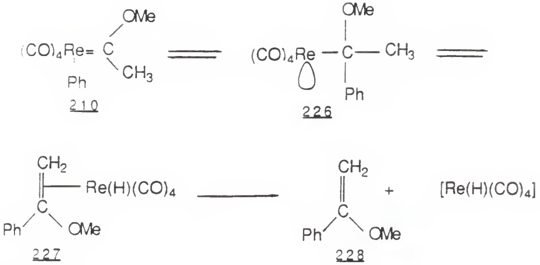


Figure 72

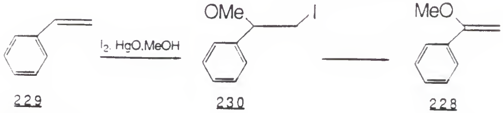


Figure 73

possible that the carbene complex is formed, but under the reaction conditions the alkyl migration is rapid, the equilibrium in this case resting heavily on the side of the unstaurated alkyl complex 226. See Figure 72. Once the sixteen electron intermediate is formed, one possible reaction which can take place is beta-hydride elimination. We know from previous work with iron, tungsten, and manganese systems that identification of specific organic products is clear evidence for the presence of the sixteen electron intermediate. (See Figure 12.) Crowther worked with the alpha-methoxycyclobutyl manganese acyl 52 as shown in Figure 13. Upon thermolysis, the carbene complex was not observed. Instead, methoxycyclobutane, 1-methoxycyclobutene, and 1,1-methoxycyclobutane carboxaldehyde were isolated. The presence of these types of organic products, then, could serve as an indication of the presence of the carbene complex 210. In the case of the noncyclic, rhenium carbene complex, subsequent to rearrangement, beta-hydride elimination from the sixteen electron intermediate would generate alpha-methoxystyrene as shown in Figure 72. Isolation and identification of this material would be evidence for the presence of 210.

Alpha-methoxystyrene was, therefore, made using a known literature preparation as shown in Figure 73.[52] Its spectra in d_6-acetone, however, did not compare to any of the materials found in the alkylation reactions nor was it observed when the volatile materials were directly removed from the crude reaction mixtures. It was important to independently prepare the alpha-methoxystyrene since we also wanted to make sure it was stable under our reaction conditions. This failed to be the case. During the decomposition we also looked for the presence of a rhenium hydride species such as 227 in the ^{1}H NMR. Metal hydride compounds have proton resonances for the hydrogen attached to the metal center at very high field, in the region -10--20ppm. No resonances were observed in the decomposition mixtures which suggested the presence of this type of compound. The absence of beta-hydride elimination was very surprising and may indicate that the reactions involved in the alkylation step were not as we had hoped: thus, the question remained, are we actually forming the alkoxy substituted carbene complex?

Although it was expected that methylation of the lithium salt of the carbene would be at the oxygen, it is also possible that methylation could occur at the metal center. Resonance structures of the carbene complex show the electron density of the anion to be distributed between the metal center and the oxygen. See Figure 74. Alkylation at the metal center of these types of species is fairly common. Therefore, we could not, a priori, exclude this possibility.[53] The peak at 280 ppm, then, could certainly be the metal alkylated, acyl compound 231, although, literature accounts of most acyl species show CO

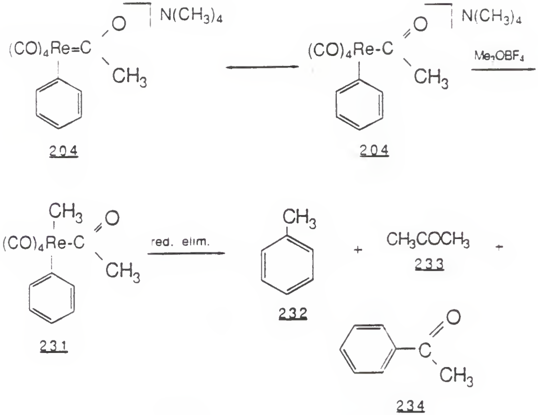


Figure 74

resonances significantly upfild from this value. However, it must be added that direct analogies to the type of compound proposed here could not be found. We, therefore, searched for organic products that would be expected to originate from 231. In Figure 74 is shown one example of how the metal alkylated species might decompose. This kind of reaction is not new; in fact, for metal centers with alkyl and acyl groups adjacent to one another, this chemistry is well known.[39,54] Searching the reaction mixtures for residues of toluene, acetone, or acetophenone proved to be unsuccessful. The reaction mixtures did not appear to contain these organic products. Also, intermediate 231 would be expected to show a strong resonance at or above 0.00 ppm in the ^1H NMR. (The protons of the methyl group which are directly attached to a metal appear at fairly high field. For example, the methyl protons in $(CO)_5ReCH_3$ appear at 0.0 - -1.0 ppm.) In the crude reaction mixtures, no significant resonances were found in this region.

Where Do We Go From Here?

Looking at the results just described it is difficult to say exactly what is occurring in these reactions. Even more discouraging when studying the ^{13}C NMR data of the decomposition mixtures are the multiple carbonyl resonances from 185-200 ppm. These peaks indicate significant metal decomposition and a multitude of metal containing products. From these results, the methylation step is either not occurring as expected or the methylation reactions are successful but the decomposition of the carbene complex is more complicated than expected. The ^{13}C NMR resonance at 280 ppm is an intriguing one since it is very characteristic of the types of carbene complexes in which we are interested. Despite this, it would still be interesting to use other alkylating agents. Of particular interest would be trimethylsilyltriflate since it should be more "oxophilic" than Me_3OBF_4 and might show a greater tendency to react at the oxygen center. These reactions will be explored by future workers in this group. Suffice it to say that although alternative routes for the alkylation step look promising, attempts to prepare the desired carbene complex 210 using the conditions we have explored throughout this paper were not successful.

CHAPTER 5
EXPERIMENTAL

Background

All manipulations containing transition metal complexes were done under N_2 or argon using Schlenck line or glove box techniques. Tetrahydrofuran, heptane, and diethyl ether were distilled from Na, and methylene chloride was distilled from P_2O_5. Hexane was distilled from CaH and acetone was dried over boron anahyride, degassed, and distilled before use. All chromatography was done under N_2 pressure using degassed 230-400 or 100-200 mesh silica gel or activity III, neutral alumina. NMR were performed using Varian XL-200 and VXR-300, and GE QE-300 spectrometers. Atlantic Microlabs performed all elemental analyses. The University of Florida completed all mass spectra. $(CpRu(CO)_2)_2$[55], $CpRu(CO)_2Na$[56], $CpW(CO)_3Na$[57], $CpW(CO)_3CH_3$[58], $CpW(CO)_3(CH_2)_3Br$[59], $CpW(CO)_3(CH_2)_3I$[60], $(CO)_5ReNa$[61], $(CO)_5ReCOPh$[47], $(CO)_5RePh$[47], $[(CO)_4Re(COCH_3)(Ph)]-[Li]+$[47], $[(CO)_4Re(COCH_3)Ph]^-[N(CH_3)_4]^+$[47], 1-methoxycyclobutenyl acid chloride[12], 1-phenylcyclopropane carbonyl chloride[16] were prepared according to known proceedures. $Ru_3(CO)_{12}$, $W(CO)_6$, and $(Re(CO)_5)_5$ were used as obtained from Strem. CH_3I and PhCOCl were distilled before use. $Br(CH_2)_3Br$ was used as obtained from Aldrich.

Preparation of Iron Complexes

1-Carbonyl(h^5-Cyclopentadienyl)(2-Methoxy)1-Ferraindene. (75)

a) To 0.135 g (0.389 mmol) dicarbonyl)(h^5-cyclopentadienyl)-(o-bromobenzyl)iron (131) in 25 ml diethyl ether at -78^{0}C was added 0.46 ml (2 equiv.) t-butyllithium. The reaction turned a dark purple and was stirred for one half an hour. The reaction was then stirred at room temperature for one hour where a dark precipitate was observed. The solvent was evaporated.

b) To the residue from a) was added 20 ml acetone and the solution was cooled to -78^{0}C. This cooled solution was added to 0.06g (0.389 mmol) Me_3OBF_4 at -78^{0}C. The reaction was stirred at -78^{0}C for 20-30 minutes where the reaction darkened. This was warmed to 0^{0}C for 15 minutes and then to room temperature for one half an hour. The solution then became dark green in color. The solvent was evaporated and the residue flash chromatographed on 230-400 mesh silica gel. Using 100% hexane, a green band was removed first, this being the carbene complex, 75. Using 30% ethyl acetate/hexane, a yellow band followed (starting material). Subsequent to this was a brown band which was not identified. ^{1}H and ^{13}C spectra compare to that reported for 75.[12]

Thermolysis of 1-Carbonyl(h^5-Cyclopentadienyl)(2-Methoxy)-1-Ferracyclopentene.

A few mgs of the carbene complex (prepared by Yang) was dissolved in C_6D_6 in an NMR tube fitted with a stopcock. The sample was freeze-thawed to degas the mixture and the tube was sealed. The tube was then immmersed in an oil bath at 100^{0}C for several hours where it went from a red to a brown color. The solution was put into a flask and the volatile materials removed and collected in a N_2 cooled trap. The volatile materials were analyzed by ^{1}H NMR and were found to contain large amounts of methoxycyclobutane and 1-methoxycyclobutene. (Their identification was made by comparing the mixtures to known samples prepared by Crowther in this group.)

Preparation of Ruthenium Complexes

Dicarbonyl(h^5-Cyclopentadienyl)(1-Phenylcyclopropanoyl 1-carbonyl)ruthenium. (87)

a) To 0.300g Na in 3.00ml Hg, was added 0.50g (1.13 mmol) Rp_2 in 150 ml THF. The reaction was stirred for 5 hrs.

b) To 0.30g (1.85 mmol) 1-phenylcyclobutanecarboxylic acid in 15 ml diethyl ether was added 0.50 ml oxalyl chloride. The mixture was stirred overnight. The solvent was evaporated and the residue used directly.

c) To the residue in b) added to 10 ml THF at room temperature was added the solution from a). The reaction was stirred overnight. The solvent was then evaporated and the residue dissolved in a 50/50 ethyl acetate/hexane mixture and the solution filtered over Celite. The solvent was then evaporated and the residue put on a silica gel (200-430 mesh) column and flash chromatographed with 20% ethyl acetate/hexane. The acyl complex was left on top of the column as a red band. After eluting and discarding three other materials off the column, the red band was brought down with 50% ethyl acetate/hexane and isolated as a brown/red oil, 0.20g (29%). IR(C_6D_6): 2026.5 cm^{-1}, 1965.3 cm^{-1}, 1637.0 cm^{-1}. ^1H NMR(C_6D_6): 0.65-0.70 ppm (2 H, CH_2, m), 1.29-1.35 ppm (2 H, CH_2, m), 4.32 ppm (5 H, Cp, s), 6.80-7.18 ppm (4 H, aryl, m). ^{13}C NMR(C_6D_6): 15.01 ppm (CH_2), 54.08 ppm (CH_2), 88.91 ppm (Cp), 127.07 ppm, 128.57 ppm, 131.36 ppm, 142.507 ppm (aryl), 200.63 ppm (terminal CO), 233.58 ppm (CO). (See Figure 75.)

Dicarbonyl(h^5-Cyclopentadienyl)(1-methoxycyclobutenoyl-1-carbonyl)ruthenium. (86)

a) The Rp anion was prepared as described above using 0.50g (1.13 mmol) Rp_2 in 100ml THF.

b) To 0.40g (2.25 mmol) 1-methoxybenzocyclobutenyl carboxylic acid in 15 ml diethyl ether was added 0.6 ml oxalyl chloride. The reaction was stirred overnight. The solvent was evaporated and the residue used without further purification.

c) To the residue from b) was added the solution from a) at room temperature. The mixture was stirred overnight. The solvent was evaporated and the residue dissolved in 50% ethyl acetate/hexane solution and filtered over Celite. The solvent was evaporated and the residue flash chromatographed on neutral alumina, activity III. The first broad yellow band was collected in two halves the first containing ruthenocene and the second the desired acyl complex. The solvent was evaporated and the remaining solid recrystallized from acetone/hexane. A yellow, crystalline solid was collected, 0.22g, 23%. m.p.= 84.5-86.0^{0}C. IR(CH_2Cl_2): 2030.6 cm^{-1}, 1970.7 cm^{-1}, 1635.6 cm^{-1}. ^{1}H NMR(C_6D_6, 300 MHz): 3.13-3.17 ppm (1H, d, CH), 3.25 ppm (3H, s, OCH_3), 3.72-3.77 ppm (1H, d, CH), 4.65 ppm (Cp), 7.97-7.29 ppm (4H, m, aryl). ^{13}C NMR(C_6D_6, 75 MHz): 38.14 ppm (CH_2), 52.45 ppm (OMe), 89.94 ppm (Cp), 97.18 ppm (C), 123.79 ppm, 127.01 ppm, 129.55 ppm, 143.30 ppm, 145.67 ppm (Aryl), 201.47 ppm (CO, terminal), 237.09 ppm (CO, acyl). MS (HR): 382.9916, (Theoretical: 382.9947). MS (EI): 251 ($-CORuCp(CO)_2$), 223 ($-RuCp(CO)_2$). (See Figure 76.)

Dicarbonyl(h^5-Cyclopentadienyl)(3-Bromo-1-propyl)Ruthenium. (134)

a) To 0.200g (8.70mmols) Na was added 2.00ml Hg. To the amalgam was added 0.41g (0.923 mmol) Rp_2 in 150ml THF. The solution was then stirred for 3-5 hrs.

b) To 0.41g (2.03 mmols) $Br(CH_2)Br$ in 20 mls THF at -78°C was added the solution from above. The mixture was warmed to room temperature and stirred overnight. The solvent was then removed in vacuo and the remaining residue extracted three times with 10 ml portions of hexane. The hexane was then removed leaving an orange oil. The solid was dissolved in hexane and cooled to -78°C where crystals were formed. The hexane was removed by filter cannula and the remaining residue evacuated leaving a yellow oil (90-95%). The oil can be further recrystallized in hexane at -30°C which at room temperature becomes an oil. IR (Hexane): 2021.7 cm^{-1}, 1932.4 cm^{-1}. ^1H NMR(C_6D_6, 75 MHz): 1.37-1.44 ppm (2 H, CH_2, t), 3.05-3.10 ppm (2 H, CH_2, m), 4.47 ppm (5 H, Cp, s). ^{13}C NMR(C_6D_6, 75 MHz): -6.96 ppm (CH_2), 36.21 ppm (CH_2), 42.91 ppm (CH_2), 88.41 ppm (Cp), 202.46 ppm (CO). $C_{10}H_{11}O_2RuBr$ calcd. for 134: C, 34.30; H, 3.23. Analysis Found: C, 34.23; H, 3.20. (Note: Neither MS(EI) nor (CI) could be obtained for 134. (See Figure 77.)

Dicarbonyl(h^5-Cyclopentadienyl)(3-Iodo-1-propyl) ruthenium.(135)

To 0.48g (1.40 mmols) dicarbonyl(h^5-cyclopentadienyl)-(3-bromo-1-propyl)ruthenium in 15 ml acetone was added 0.63g (4.3 mmols, 3 equiv) NaI in 150-200 mls acetone. The solution became cloudy after 30 minutes but was complete only after overnight stirring. The solvent was then evaporated in vacuo and the residue extracted three times with 15 ml portions of hexane. The hexane was then removed leaving a yellow solid. The solid was then dissolved in hexane and cooled to -78^0C. A solid reprecipitated giving 0.35g (0.90 mmol) of the product (64%). This solid was then recrystallized from hexane at -30^0 C, leaving a pale yellow crystalline solid. Only the crystalline material was used for the synthesis of 138. m.p.= 38.0-39.0^{0}C. IR(Hexane): 2022.9 cm^{-1}, 1965.2 cm^{-1} (CO). ^{1}H NMR(C_6D_6, 75 MHz): 1.36-1.42ppm (2 H, CH_2, t), 1.86-1.98ppm (2 H, CH_2, m), 2.81-2.88ppm (2 H, CH_2, t), 4.40 ppm (5 H, s, Cp). ^{13}C NMR(C_6D_6, 75 MHz): -4.24ppm (CH_2), 10.00ppm (CH_2), 43.93ppm (CH_2), 88.38ppm (Cp), 202.47ppm (CO). $C_{10}H_{11}O_2RuI$ calcd for 135: C, 30.70; H, 2.84. Analysis Found: C, 30.83; H, 2.80. (Note: Neither MS(EI) nor (CI) could be obtained for 135. (See Figure 78.)

Preparation of 1-Carbonyl-(h^5-Cyclopentadienyl)(2-Methoxy)-1-Ruthenacyclopentene.

a) To 0.20g (0.512mmol) dicarbonyl(h^5-cyclopentadienyl)(3-iodo-1-propyl)ruthenium in 60-80 ml Et_2O cooled by a hexane/N_2 bath at -100^0C was added 0.64 ml (2.1 equiv.) of a 1.7M solution of t-Butyllithium. The temperature of this lithiation was found to be important. At temperatures as high as -78^0C significant decomposition occurred. The alkyl lithium reagent was added over a 15 minute period. The reaction was allowed to stir at the bath temperature and was warmed to room temperature as the hexane slush warmed slowly over several hours. The color of the solution went from a yellow solution at low temperature to a light yellow color with a whitish solid at room temperature. At times the solution darkened to a brown color with a whitish solid. The solution was stirred at room temperature overnight. The amount of time the reaction was stirred at room temperature was also found crucial in that adequate time is required for ring closure.

b) After stirring overnight, the ether was evaporated and the solid residue was redissolved in rigorously dried acetone. (The acetone was dried over 4 A molecular sieves, distilled, dried over B_2O_5, and subsequently degassed by freeze-thawing.) This solution was cooled to -78^0C and added to 0.08g (0.512mmol, 1 equiv.) Me_3OBF_4 also cooled to -78^0C. (The Me_3OBF_4 was found to be reactive to acetone at room temperature, therefore, the Me_3OBF_4 is not dissolved in the acetone prior to addition.) The solution was stirred at -78^0C for half an hour, warmed to room temperature and stirred for one half-one hour. The solvent was then evaporated to give a yellow/brown solid.

c) The carbene complex can be purified by dissolving the above yellow/brown residue in hexane and flash chromatographing over 100-200 mesh silica gel or activity III, neutral alumina. The first, fast moving yellow band was collected and found to be the desired carbene complex. If necessary, further purification can be obtained by flash, chromatography on 230-400 mesh silica gel with 10% methylene chloride/hexane. Again the first yellow band was collected. The carbene can be isolated in 20-25% yield. (The material can also be sublimed at 30.0^0C. This will remove most impurities. In order to remove unreacted starting material, column chromatography was run as stated above with the exception that the yellow band was collected in two fractions the first portion being enriched in the carbene complex and the trailing fraction being enriched in the alkyl iodide. This can be done several times until the initial parts of the band are clean. Several sublimations will also remove the iodide because even though a portion of it will sublime with the carbene (even at room temperature), the sublimate will be enriched with the carbene complex. Attempts to recrystallize from hexane at -30- -78^{0}C did not give a crystalline solid.) IR(hexane): 1943 cm^{-1}. ^{1}H NMR(C_6D_6, 300MHz): 1.68-2.04 ppm (2H, m, CH), 2.10-2.20 ppm (1H, m, CH), 2.36-2.47 ppm (1H, m, CH), 2.51-2.68 ppm (1H, m, CH), 2.79-2.88 ppm (1H, m, CH), 3.74 ppm (3H, s, OMe), 4.73 ppm (5H, s, Cp). ^{13}C NMR(C_6D_6, 75 MHz): 7.65 ppm (CH_2), 31.39 ppm (CH_2), 60.13 ppm (OMe), 86.89 ppm (Cp), 207.92 ppm (CO), 325.02 ppm (carbene). $C_{11}H_{14}O_2Ru$ calcd for 138: C, 47.31; H, 5.02. Analysis Found: C, 47.40; H, 5.10.

Reactions of Ruthenium Complexes

Thermolysis of Dicarbonyl(h^5-Cyclopentadienyl)(1-Methoxy benzocyclobutenoyl-1-carbonyl)ruthenium.

Approximately 100mg of the acyl complex was dissolved in C_6D_6 in an NMR tube. The tube was put in an oil bath and heated to 85^{0}C. After four days the reaction was complete and virtually quantitative by NMR. After several successive recrystallizations (to remove the acyl complex and some ruthenocene which were formed in small quantities upon heating) in hexane at -30^{0}C, a yellow solid was obtained. m.p.= 79-81^{0}C. ^{1}H (C_6D_6, 300 Mhz): 3.58 ppm (3H, s, OMe), 4.70 ppm (5H, s, Cp), 4.79 ppm (2H, s, CH_2), 6.80-7.30 ppm (4H, m, aryl). ^{13}C ($CDCl_3$, 75 MHz): 60.17 ppm (CH_2), 69.15 ppm (OMe), 88.25 ppm (Cp), 116.44 ppm (CR_2=), 123.57, 124.65, 127.77, 128.47, 147.99, 158.46 ppm (aryl), 199.65

(CO). MS(EI): 383 (M+), 355 (M+ - CO), 328 (M+ - 2CO). (It is interesting to note here that the 1-methoxybenzocyclobutenyl methyl ester was also heated to 85^{0}C in C_6D_6. The reaction mixture showed several products being formed and they were not identified. This experiment serves to show the inherent instability of these ring systems at high temperature.) (See Figure 79.)

Photolysis of Dicarbonyl(h^5-Cyclopentadienyl)(1-Methoxy-Benzocyclobutenoyl-1-carbonyl)ruthenium.

a) Approximately 50 mg of dicarbonyl(h^5-cyclopentadienyl)(1-methoxybenzocyclobutenoyl-1-carbonyl)ruthenium was dissolved in C_6D_6 in an NMR tube with a boiling chip. Photolysis (450 W, Hg lamp) was done with sonication and followed by ^{1}H NMR. No reaction was observed after several hours.

b) The above reaction was repeated, however, THF was used as a solvent instead of C_6D_6 and the reaction was again followed by ^{1}H NMR. (Aliquots were taken, the solvent evaporated, and the residue redissolved in C_6D_6.) Again, no reaction was observed after 20 hours.

Reaction of Dicarbonyl(h^5-Cyclopentadienyl)(1-Methoxy-benzocyclobutenoyl-1-carbonyl)ruthenium with Trimethylamine Oxide.

To 10mg of the acyl complex dissolved in d_6-acetone in an NMR tube was added 0.003g (0.027 mmols) trimethylamine oxide (dried by azeotropic distillation of the water with benzene and subsequent evacuation). By ^{1}H NMR, significant decomposition was seen but there was no indication of the desired product.

Photolysis of Dicarbonyl(h^5-Cyclopentadienyl)(1-Phenyl-cyclopropanoyl-1-carbonyl)ruthenium.

a) The acyl complex was dissolved in d_6-acetone in an NMR tube and photolyzed (450W, Hg lamp) with sonication at room temperature for twelve hours. The reaction was followed by ^{1}H NMR; no reaction was seen. b) To the solution from above was added an excess of P(Ph)$_3$. The reaction was followed by ^{1}H NMR and some reaction was observed. After flash-chromatography on 230-300 mesh silica gel with 10% ethyl acetate/hexane, a yellow band was eluted first and found to be starting material. Using 20% ethyl acetate/hexane a orange band was eluted and found to be a complex mixture of materials in very small yield.

Reaction of 1-Carbonyl(h^5-Cyclopentadienyl)(2-Methoxy)-1-Ruthencyclopentene with P(Ph)$_3$.

To a solution of the carbene complex in d_6-acetone in an NMR tube was added 2 equiv. P(Ph)$_3$. This was left overnight and no reaction was found. The solvent was then evaporated, C_6D_6 was added, and the reaction was heated to 70^{0}C for 24 hours. No reaction was observed by ^{1}H NMR.

Reaction of 1-Carbonyl(h^5-Cyclopentadienyl)(2-Methoxy)-1-Ruthenacyclopentene with $P(CH_3)_3$.

To a solution of the carbene complex in C_6D_6 was added XS of $P(CH_3)_3$. After two days at room temperature a complex mixture of products was observed by ^1H NMR.

Reaction of 1-Carbonyl(h^5-Cyclopentadienyl)(2-Methoxy)-1-Ruthenacyclopentene with CO.

a) The carbene complex was dissolved in 0.1 ml C_6D_6 in a thick walled NMR tube fitted with a stopcock and adaptor. To this was added 6 atm of CO (CO was added via the Schlenck line measuring the volume of the apparatus and the pressure difference upon addition of the CO gas to an evacuated NMR tube cooled with liquid N_2.). After one month, no reaction was observed at room temperature as monitored by ^1H NMR.

b) Two more reactions were made as above and charged with 6.5 and 7 atms of CO. These were heated to 98^{0}C. After 13 days, no reaction was observed by ^1HNMR.

Reaction of 1-Carbonyl(h^5-Cyclopentadienyl)(2-Methoxy)-1-Ferracyclopentene With CO.

A few mg of 1-carbonyl(h^5-cyclopentadienyl)(2-methoxy)-1-ferracyclopentene was dissolved in C_6D_6 and pressurized with 4.5 atmosphere of CO using the same procedure and apparatus as above. The reaction was followed by TLC and after 24 hours showed the formation of Fp_2, the sigma complex 27, and unreacted carbene. These were verified by reports of Stenstrom.[62] Reaction was 30-40% complete by NMR.

Reaction of 1-Carbonyl(h^5-Cyclopentadienyl)(2-Methoxy) -1-Ruthenacyclopentene with $NaOCD_3$ in CD_3OD.

a) To 16 mg (0.055 mmol) of the carbene complex was added 0.3ml of a 0.24 M solution of toluene in CD_3OD in a thick walled NMR tube fitted with a stopcock.

b) To the solution from a) was added 0.05 ml of a $NaOCD_3$ solution made by adding 0.065g (0.651 mmol) Na to 3.0 ml CD_3OD. The reaction was monitored by ^1H and ^{13}C NMR. As shown in Figures 36 and 37 at room temperature only methoxide exchange occurred. The NMR tube was then immersed in an oil bath and heated to 85^{0}C. The reaction was again monitored by NMR and an unknown product was formed. No attempt was made to identify the new material.

Reaction of 1-Carbonyl(h^5-Cyclopentadienyl)(2-Methoxy) -1-Ruthenacyclopentene with Lithium Diisopropylamide.

a) To 0.03g (0.107 mmol) of the carbene complex in 30 ml THF at -78^{0}C was added 0.44 ml (1.5M, 6 equiv.) lithiumdiisopropyl amide. The solution turned from a bright yellow to colorless. This was stirred for one half an hour. (Several experiments were tried with this reaction so as to generate almost complete disubstitution. The literature preparation called for 3 equiv. of LDA to be added to a -

78^0C solution of THF. This was stirred for ten minutes and then quenched at -78^0C. It was found with this particular carbene complex, to get a thorough exchange of the protons adjacent to the carbene carbon, the reaction was warmed to room temperature before quenching. This does not appear to give significant decomposition. The amount of LDA was varied from 3-6 equivalents.)

b) The solution from a) was warmed to room temperature and 0.8 ml CD_3OD was added to the mixture. Upon addition, the solution became immediately bright yellow in color. This was stirred for several minutes. The solvent was evaporated and the carbene complex column chromatographed on silica (230-400 mesh) eluted with 10% ethyl acetate/hexane. The yellow band was collected and the residue dissolved in benzene and put in a thick walled NMR tube fitted with a stopcock. The tube was then evacuated, degassed, and sealed. (70%) See Figures 41 and 42.

c) The tube was allowed to stand at room temperature for two days; no reaction was observed. The tube was then heated to 63^0C for four hours; no reaction was observed. The temperature of the bath was increased to 100^0C and the reaction monitored for 3 days. After 24 hours, no reaction was observed. After this point, however, as shown in Figures 46 and 47 proton exchange for the deuterium was occurring. The reaction was discontinued as water was assumed to have contaminated the reaction.

Preparation of Tungsten Complexes

Tricarbonyl(h^5-Cyclopentadienyl)(3-Iodo-1-propyl) Tungsten.(185)

To 0.50 g (1.10 mmols) tricarbonyl(h^5-cyclopentadienyl) (3-bromo-1-propyl)tungsten in 25 ml acetone was added 0.30 g (2 equiv) NaI in 100 ml acetone. After 10 minutes the solution became cloudy. In three hours the solvent was evaporated and a crude ^{1}H NMR taken showing the reaction to be incomplete, therefore, another 0.30 g NaI was added and the reaction was stirred overnight. The solvent was evaporated and the residue dissolved in hexane and filtered over Celite. The solvent was evaporated and the residue flash chromatographed on silica gel with 40% ethyl acetate/hexane. The column needs to be run quickly as the iodide can decompose to a greenish compound. The first yellow band was collected and the solvent evaporated leaving a yellow solid. The alkyl bromide and iodide must be kept refrigerated when stored. Even as solid materials, in the dry box, decomposition can be observed at room temperature. (50%) (It is important to note here that the results of this experiment are not necessarily consistent. Yields varied from 10-50%. The above report is a description of the best

trial.) ^{1}H NMR (C_6D_6, 300 MHz): 0.9-1.0 ppm (2 H, m, CH_2), 1.55-1.68 ppm (2 H, m, CH_2), 2.50-2.60 ppm (2 H, m, CH_2), 4.12 ppm (Cp). ^{13}C NMR (d_6-acetone, 75 MHz): -12.00 ppm (CH_2), 11.80 ppm (CH_2), 42.00 ppm (CH_2), 92.50 ppm (Cp), 219.5 (CO), 230.00 ppm (CO). (See Figure 80.)

Attempted Preparation of 1-Tricarbonyl(h^5-Cyclopentadienyl)(h^5-Cyclopentadienyl)(2-Methoxy)-1-Tungstacyclopentene.

a) To 0.25g (0.50 mmol) Tricarbonyl(h^5-cyclopentadienyl)(3-iodo-1-propyl)tungsten in 20 ml THF at -78^{0}C was added 0.71ml (2quiv) of a 1.4M solution of t-butyllithium. The reaction turned an orange color and after half an hour at -78^{0}C a yellow solution was observed with a yellow precipitate. The reaction was warmed to room temperature where the solid began to dissolve leaving an orange solution (some red oil was present). The solvent was evaporated leaving a golden/yellow solid.

b) The solid was then dissolved in rigorously dried acetone, cooled to -78^{0}C and added to 0.075g (0.51mmol) Me_3OBF_4 also cooled to -78^{0}C. This was stirred for one half an hour where it turned orange, warmed to 0^{0}C for one half an hour, and warmed to room temperature for 45 minutes. The solvent was evaporated, the residue dissolved in hexane and flash-chromatographed on 100-200 mesh silica gel. The first yellow band was collected giving 72% yield of a yellow solid which was $CpW(CO)_3CH_3$. (These results shown in this experiment are consistent and reproducible.)

Reactivity of Tungsten Complexes

Reaction of $CpW(CO)_3CH_3$ with MeLi.

To 0.20g (0.57 mol) in 30 ml Et_2O at -78^0C was added 0.38ml (1 equiv.) of a 1.5M solution of MeLi. This was stirred at -78^0C for 15 minutes, warmed to room temperature, and followed by IR. After 3 hours no reaction was seen.

Reaction of $CpW(CO)_3CH_3$ with PhLi.

To 0.20g (0.57 mol) in Et_2O at -78^0C, was added 0.38ml (1equiv) of a 1.5 M solution of PhLi. After warming to room temperature as above and stirring overnight, IR showed no reaction. To this solution at room temperature was added one more equiv. of PhLi. IR showed formation of some Wp_2. Workup gave only starting material.

Reaction of WpNa with Me_3OBF_4.

a) To 0.2g Na metal was added 0.8ml freshly distilled cyclopentadiene. This was stirred overnight.

b) To 2.60g (7.25mmol) $W(CO)_6$ in 100ml THF was added the solution from above. This was refluxed overnight, cooled to -78^0C, and added to 1.10g (1 equiv.) Me_3OBF_4. The reaction was warmed to room temperature where it turned an orange color. After stirring for 1.5 hours, the solvent was evaporated leaving a yellow solid which was identified as $CpW(CO)_3CH_3$. No yield was determined.

Identification of Cyclopropane from Reaction of $Wp(CH_2)_3I$ with t-Butyllithium.

a) To 0.20 g (0.398 mmol) $Wp(CH_2)_3I$ in 15 ml diethyl ether at -78^0C was added 0.50 ml (1.7 M, 2.0 equiv.) t-butyllithium in a closed reaction vessel. This was stirred for 20 minutes at -78^0C and warmed to room temperature and stirred for one half an hour. The solvent was then evaporated and collected in an N_2 trap fitted with a stopcock. The solution was then analyzed by gas chromatography. The chromatograms showed a peak with a retention time of 1.66 minutes (cyclopropane) and 2.03 minutes (diethyl ether). (Gas chromatography was performed on a Varian 3400 GC, 3% OV-210-2mX1/4" SS column.) The retention times and elution were compared to some standard solutions of cyclopropane in diethyl ether. The solutions from the reactions were also enriched in cyclopropane to further identify the cyclopropane peak in the GC.

b) To the residue from a) was then added 20 ml THF. This was cooled to -78^0C and 10 ml CH_3I (3XS) was added. The reaction was warmed to room temperature for one half an hour. The solvent was evaporated and NMR of the residue showed a virtual quantitative yield of $WpCH_3$.

Attempted Photolysis of $WpCH_3$ in Acetonitrile.

A few mg of $WpCH_3$ was dissolved in d_3-acetonitrile in an NMR tube with a boiling chip. The mixture was photolyzed (450 W, Hg lamp) with sonication and after a few minutes the solution darkened in color. ^1H NMR already showed a significant number of new products. Futher photolysis worsened the mixture. No attempt was made to identify the material although the red color indicated Wp_2.

Preparation of Rhenium Complexes

Modification of the Preparation of (Pentacarbonyl)(Benzoyl-1-Carbonyl)Rhenium and (Pentacarbonyl)(Benzoyl)Rhenium.

The procedure was used as reported by Heiber[8] with the exception of the purification of the acyl and sigma complexes. Once the acyl complex was made, it was sublimed from the reaction mixture, removing it from NaCl. If the sublimate was an oily residue, it was triturated in diethyl ether for several hours or overnight giving a solid suspended in the solvent. The mixture was then cooled to -78^0C and filtered. The solid, yellow residue remaining was sublimed at 0.025 mm, $100-110^0C$. This clean sublimate is then sublimed 125^{0c} several times. This temperature will decarbonylate the acyl, 224, and generate the sigma complex, 206. The initial sublimates will contain both the acyl and the sigma complex. Eventually, after three to four sublimations the acyl will be reacted and only the sigma complex will remain. (Care must be taken not to exceed this temperature as decomposition of these materials will occur.) Again, after triturating the sigma complex in diethyl ether and cooling the residue to - 78^{0}C, the solvent was removed by filtration leaving very pure 206. It should be noted that the acyl and sigma complexes are both slightly soluble in diethyl ether, therefore, only small amounts of solvent should be used and the reaction only filtered at -78^{0}C.

Attempted Preparation of Tetracarbonyl (1-Phenyl)(2-Methoxy)(2-Methyl)-1-Rhenium.

a) To 0.71g (1.76 mmol) $(CO)_5$RePh in 20ml THF at -78^{0}C was added 1.83ml (1.45 equiv.) of a 1.4M solution of MeLi. This was stirred at -78^{0}C for 1.25 hours, warmed to room temperature and the solvent was evaporated.

b) To 0.26g (1 equiv) Me_3OBF_4 was added the residue from a) at -78^{0}C dissolved in d_6-acetone (rigorously dried). The reaction was followed by ^{1}H and ^{13}C NMR. After reaction was complete (several hours), several attempts were made to purify the reaction mixture. The residue was evaporated and the volatiles collected. The nonvolatile material composed the majority of the mixture. Products could not be separated by column chromatography (silica or neutral alumina (III)) as they remained on top of the column and could not be removed even with solvents such as THF. The materials were fairly insoluble in most solvents except THF and acetone. Attempts were made to crystallize the products in THF/hexane or acetone/hexane mixtures. These, however, left only orange oils which were still very complex.

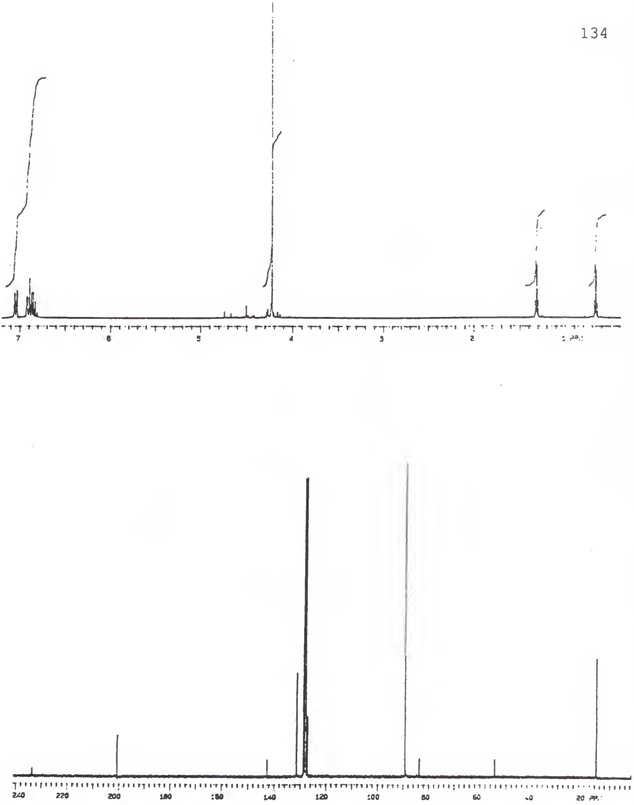


Figure 75: ^{1}H and ^{13}C NMR of Dicarbonyl(h^{5}-Cyclopentadienyl)(1-Phenylcyclopropanoyl-1-carbonyl) ruthenium

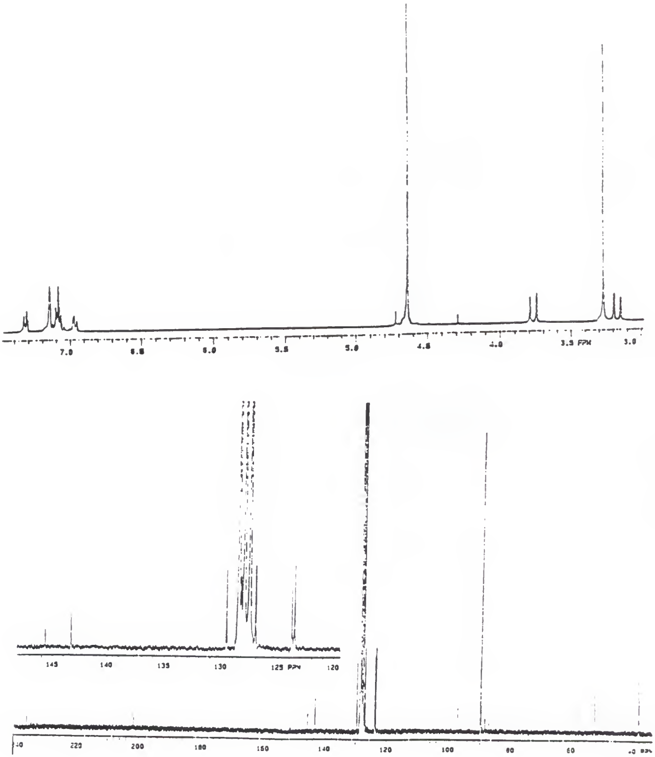


Figure 76: ^1H and ^{13}C NMR of Dicarbonyl(h^5-Cyclopentadienyl)(1-Methoxycyclobutenoyl-1-carbonyl)ruthenium.

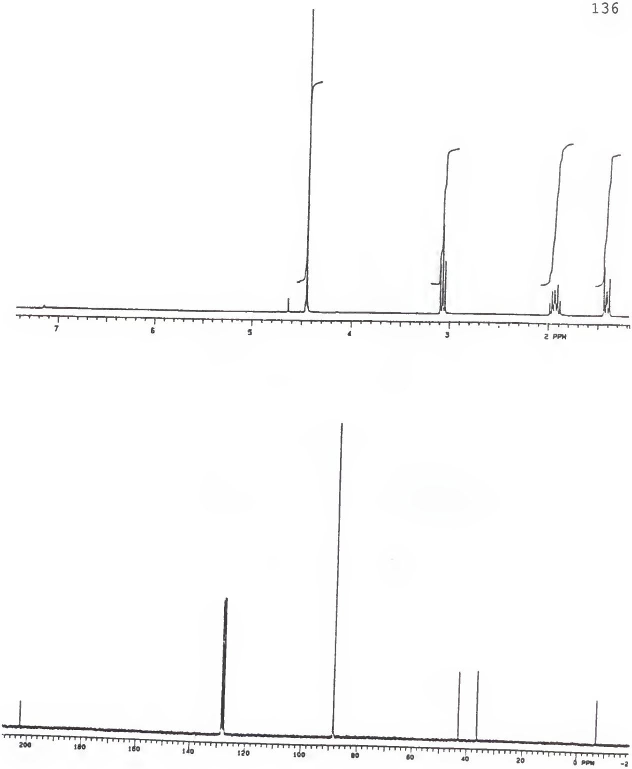


Figure 77: ^1H and ^{13}C Spectra of Dicarbonyl(h^5-Cyclopentadienyl)(3-Bromo-1-propyl)ruthenium.

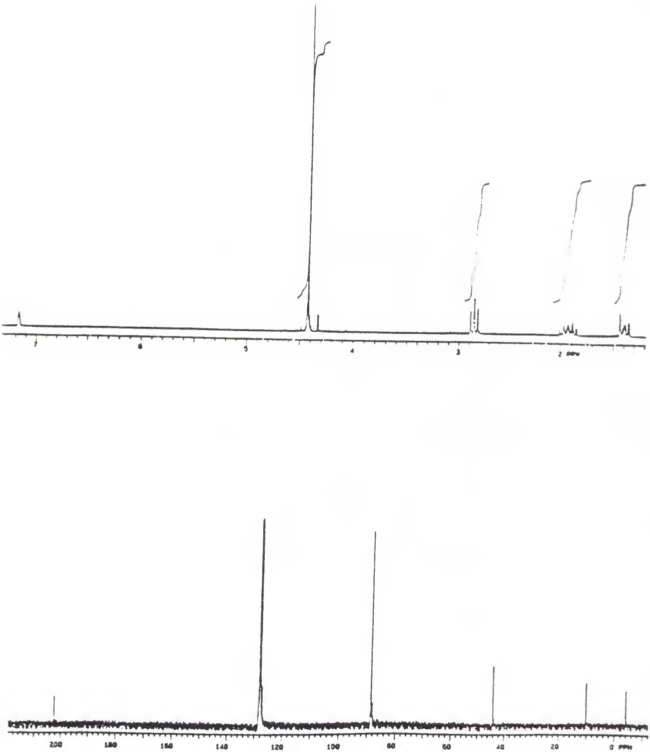


Figure 78: ^{1}H and ^{13}C Spectra of Dicarbonyl(h^{5}-Cyclopentadienyl)(3-Iodo-1-propyl)ruthenium.

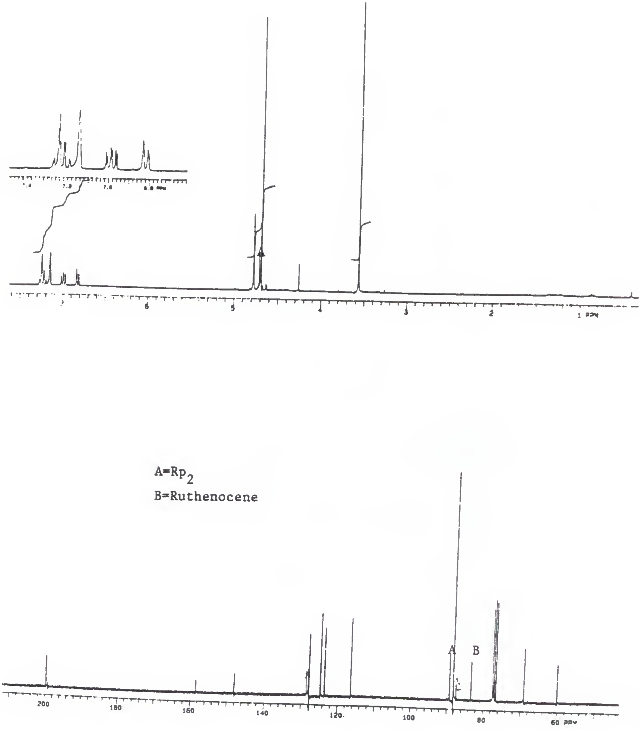


Figure 79: Thermolysis Product 100.

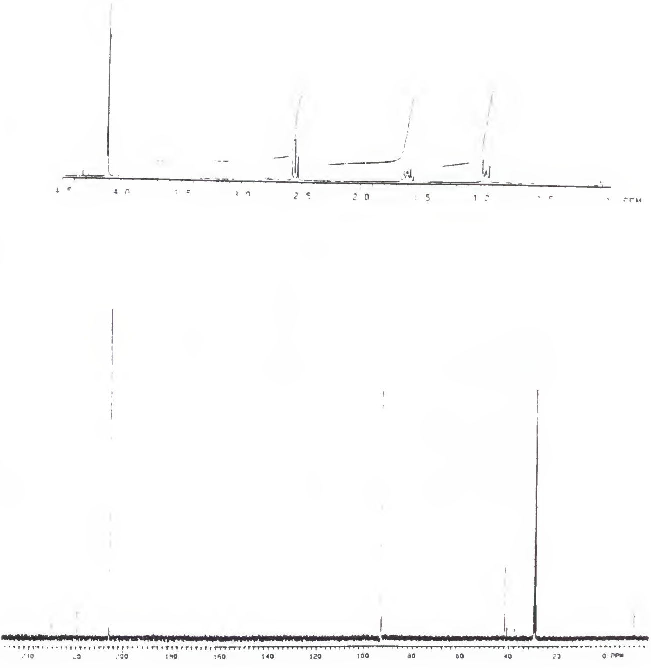


Figure 80: ^{1}H and ^{13}C Spectra of Tricarbonyl(h^{5}-Cyclopentadienyl)(3-Iodo-1-propyl)tungsten.

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